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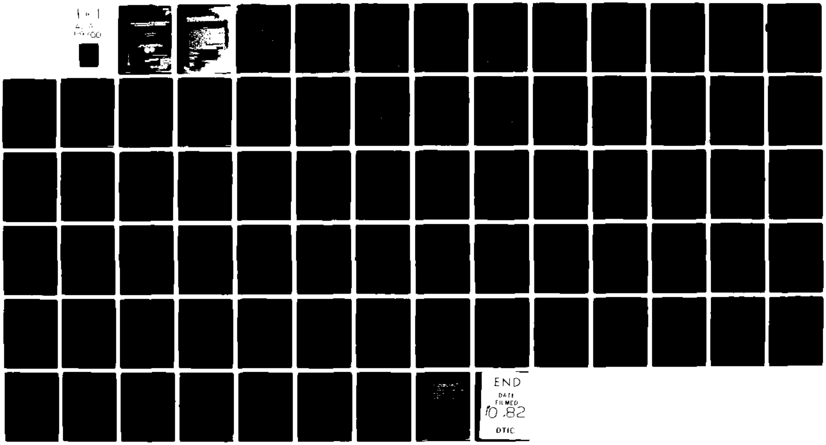

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(U) *Data Processing for the Determination of Chemical Kinetic Parameters*, by Gregory A. Vernon. China Lake, Calif., Naval Weapons Center, August 1982. 70 pp. (NWC TP 6337, publication UNCLASSIFIED.)

(U) Renewed interest in thermal analysis has stimulated development of new computer-compatible techniques for data analysis and reduction. Application of these techniques is intended for use in the determination of chemical kinetic parameters of rocket motor and warhead liners, propellants, and explosives in an effort to increase the safety of handling this hardware.

(U) The numerical methods for data reduction in the field of thermal analysis have had to be updated due to new instrumentation and increasing computer technology. Chemical kinetics subroutines have been developed for isothermal and nonisothermal differential scanning calorimetry and for differential thermal analysis by digitizing analog outputs. Mathematic interpretation of thermodynamic data is accomplished with application of the Gibbs-Helmholtz equation.

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INTRODUCTION

The determination of physical properties of liners, explosives, and propellants is important for the characterization of cook-off behavior, aging processes, and the mathematic modelling of the thermal responses of warheads and rocket motors.

The development of test hardware, data acquisition, and numerical methods for data reduction and analysis is of considerable importance. Thermal analysis techniques such as Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), and Differential Thermal Analysis (DTA) have traditionally been used to determine the thermal characteristics and decomposition kinetics of reactive substances.

As compared with other analytical techniques, thermal analysis has until recently received little attention in chemical research. This is primarily due to instrument insensitivity and the laborious task of manually reducing data. More sensitive techniques, usually spectroscopic in nature, were opted for in the determination of chemical kinetics.

There has recently been a resurgence of interest in thermal analysis due to the increased safety awareness of both the industrial and military sectors. This is due to the development of new materials for use in energy development, and for extraterrestrial and military applications.

Considerable activity has been generated in the area of the application of known numerical techniques to thermal analysis. This has been made possible with the development of new thermal analysis techniques, the availability of microprocessor-controlled analysis instrumentation, and the development of small computer technology for the acquisition and reduction of large quantities of data.

As a part of an ongoing process of upgrading the Naval Weapons Center's analytical capabilities, the Explosives Formulation Branch has written computer software to acquire and analyze data from laboratory instruments. These programs include routines to input digital data from interfaced digitizers and various numerical analysis and graphics subroutines to reduce, display, and analyze the data.

Chemical kinetics subroutines have been developed for nonisothermal DSC, isothermal DSC, and for TGA. This has been accomplished through the digitization of the analog outputs of the laboratory instrumentation which is achieved by interfacing with a Fluke 7600A scanning digital multimeter or Fluke 8520A digital multimeter. Transfer to the Hewlett-Packard 9845T computer is achieved via the IEEE-488 interface bus either by direct computer command or by use of service

request interrupts. The rate of data acquisition is programmed via command string to the microprocessor control units of the digital multimeters.

THEORETICAL BACKGROUND

Mathematical interpretation of thermodynamic data is accomplished through the application of the Gibbs-Helmholtz equation, usually stated as:

$$\frac{\partial\ \Delta G/T}{\partial\ (1/T)} = \Delta H$$

where G is the Gibbs free energy, H is the enthalpy, and T the absolute temperature. Kinetic data may be determined from the relationship $\Delta G° = -RT \ln K(T)$, K(T) being the equilibrium constant at temperature T. For a reaction such as $A \rightleftarrows B$, the equilibrium constant may be written $K(T) = k_2(T)/k_2{*}(T)$ where $k_2(T)$ is the rate of the forward reaction and $k_2{*}(T)$ is the rate of the reverse reaction.

Arrhenius first gave the expression for these rate constants as:

$$k_2(T) = Z \cdot \exp(-E{*}/RT)$$

where Z is an experimentally determined rate constant with the dimensions mole/sec and E* is the activation energy. The form of this equation was taken as a logical extension of the Gibbs-Helmholtz equation and is used presently in experimental determinations. Current interpretation of E* is that of an energy barrier or depth of a potential well, and the factor exp(-E*/RT) is the probability per unit time that a molecule will penetrate the barrier.

From the Gibbs-Helmholtz equation, the temperature dependence of the equilibrium constant is given as:

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Unfortunately, when dealing with highly energetic materials, the chemical reactions are irreversible. The temperatures and pressures are not uniform and, in fact, have severe gradients throughout the material, presenting a problem in nonequilibrium thermodynamics. When dealing with small samples, temperature and pressure gradients are usually assumed to be negligible and a rate equation may be written for the reaction. For the reaction $B \rightarrow$ Products:

$$\text{Rate} = \frac{dX}{dt} = k(T) \cdot f(X)$$

where X is the fraction of B that has reacted and f(X) is some function which depends upon the mechanism by which the reaction takes place.

For simple liquid and gaseous reactions, f(X) takes the form $(1-X)^n$, where n is referred to as the reaction order, n is usually 2 or less. A set of coupled reactions will yield fractional n's while reactions which occur in the solid state via diffusion or nucleation mechanisms take on complex algebraic forms with n usually less than 1.

When looking at energetic materials, n=1 works quite well in the higher temperature ranges where $B \rightarrow$ Products is an accurate representation of the reactions taking place. However, at lower temperatures, nucleation reactions are present. They are dependent upon the surface free energy of the material which is affected by such factors as physical state, impurities, and method of preparation. Thus, a study of reaction rates at higher temperatures may give a somewhat limited view of the manner in which a material might behave.

For nonhomogeneous materials such as propellants, reaction rates are diffusion controlled and highly pressure-dependent. For materials of current interest, f(X) will stand for (1-X) for simple reactions and X(1-X) for the autocatalytic reactions which occur in many explosives.

For materials which melt with decomposition, complex kinetics occur in the initial stages of the decomposition reaction. Behavior beyond the exotherm maximum is usually more typical of the first order reaction, $B_{(liquid)} \rightarrow$ Products. The first stages of the decomposition process frequently draw the most interest in the thermal stability studies. Investigation of this behavior will give a more complete description of how a particular substance reacts.

ANALYTICAL TECHNIQUES

GENERAL

Ordinate data points are obtained by digitizing millivolt output from the instrumentation with the sensitivity of the instruments selectable by the operator. The analog output of the DSC represents energy absorption (endotherm) or release (exotherm) in units of millicalories per second. The TGA output represents milligrams.

Abscissa data points are obtained as time from the Real Time Clock interfaced to the HP 9845T computer. Temperature is obtained as the product of time and heating rate. Extremely accurate temperature

tracking has been achieved in the case of the DSC, while less favorable results have been obtained from the TGA. This is due to the heating rates deviating from programmed values. The problem has been eliminated by manually entering data into a separate computer program after the TGA run is complete.

Data points (X_j, Y_j) are curve-fitted using a precise continuous cubic polynominal, or cubic spline, algorithm. Ordinate values are represented as:

$$Y_j = \sum_{k=0}^{3} M_{jk} \; X^k$$

where the coefficient matrix M is determined by demanding continuity of the polynominal and its first derivative at each data point.

Use of this algorithm allows facile differentiation and integration of the data curves and is relatively insensitive to noise in the instrumental output.

NONISOTHERMAL DSC

Graphics output of a DSC run of RDX Type II Class 5 is shown in Figure 1. Figure 2 is the data after a linear baseline correction has been made.

For a nonisothermal DSC run, the ordinant displacement dH/dt is given as:

$$D(t) = \Delta H \cdot \text{rate} = \Delta H \frac{dX}{dt} = \Delta H \cdot k(t)(1 - X)^n \tag{1}$$

where ΔH is the total enthalpy change for the reaction, represented as the area A, under the displacement - temperature curve. Thus dX/dt = 1/A · dH/dT. If this equation is integrated, the result is X = $\Delta Hx(T)/A$ where ΔHx is the heat released due to the fraction X reacting. This is represented by the area a(T), under the peak up until the temperature in question. Thus X(T) = a(T)/A may be determined graphically or by a numerical integration technique as is done by the computer program which has been developed (Figure 3).

Borchardt and Daniels[1] have shown that the rate constant may be expressed as:

$$k(T) = A^{n-1} \frac{dH(T)}{dt}$$

[1]Hans J. Brochardt and Farrington Daniels. "The Application of Differential Thermal Analysis to the Study of Reaction Kinetics," Journal of the American Chemical Society, Vol. 79, No. 4, July 1956, p. 41.

Comparing the rate constants at two temperatures gives:

$$\frac{k(T_2)}{k(T_1)} = \frac{(dH/dt)(T_2)}{(dH/dt)(T_1)} \cdot \left[\frac{A-a(T_1)}{A-a(T_2)}\right]^n$$

Since dH/dT is the ordinate deflection D(T), and X = a(T)/A, this relation may be rewritten:

$$\frac{k(T_2)}{k(T_1)} = \frac{D(T_2)}{D(T_1)} \cdot \left[\frac{1 - x(T_1)}{1 - x(T_2)}\right]^n$$

Assuming only one chemical reaction takes place, k(T) may be written:

$$k(T) = Z \cdot \exp(-E^*/RT)$$

and thus:

$$\frac{\exp(-E^*/RT_2)}{\exp(-E^*/RT_1)} = \exp\left[\frac{E^*}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = \frac{D(T_2)}{D(T_1)} \cdot \left[\frac{1 - x(T_2)}{1 - x(T_1)}\right]^n$$

and:

$$-E^*\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = R \ln\left[\frac{D(T_2)}{D(T_1)}\right] + nR \ln\left[\frac{1 - X(T_1)}{1 - X(T_2)}\right]$$

Thus the activation energy may be calculated from ordinate displacement and partial areas. In fact, for closely spaced data points, the last term approaches zero.[2]

The frequency factor Z, and thus the rate constant may be calculated using partial areas and known values. With ϕ as the heating rate:

$$\frac{dX(r)}{dt} = \phi \cdot \frac{dX(r)}{dT} = Z \cdot \exp\,[-E^*/RT(r)]\,[1 - \frac{a(r)}{A}]$$

In the computer implementation of this method, E* is calculated from a linear least squares (linear regression) algorithm which fits the curve of ln D versus 1/T (Figure 4).

---

[2] Jen Chiu. "Dynamic Differential Calorimetric Technique for Measuring Heat of Polymerization," in Proceedings of the Second Symposium on Analytical Calorimetry, ed. by Roger S. Porter, New York Plenum, 1970, p. 171-183.

Figure 5 shows a plot of the reaction rate versus fraction decomposed. Ideally, the plot should provide some idea of the algebraic form of the rate equation, with a straight line indicating a first order reaction. For an autocatalytic reaction, a straight line would result from plotting rate versus X(1-X). In the case of solids, there are several processes occurring simultaneously and a clear and precise interpretation of this plot would be difficult to achieve. In a homogeneous liquid, such as is present to the right of the exotherm maximum in the case of RDX, a portion may be represented by
$RDX_{(Liquid)} \rightarrow$ Products:

$$\text{Rate} = k(T)(1 - X) \tag{2}$$

and appears as a virtually linear portion of the curve. This portion may be selected for determination of kinetics for the first order reaction of Equation 2.

Kissinger[3] has devised a method based upon variable heating rates to determine the activation energy. This method is independent of reaction order and should give an accurate value for E^* assuming that only one chemical reaction is taking place at a time. The basic equation is given as:

$$d(\ln \phi/T_m)/d(1/T) = -E^*/R$$

where T_m is the temperature at which the maximum exotherm or endotherm occurs. A plot of $\ln \phi/T_m$ versus $1/T_m$ from several runs will have slope $-E^*/R$.

ISOTHERMAL DSC

The software developed for nonisothermal DSC has been modified to allow for the treatment of the isothermal case.

Because the temperature is constant in an isothermal DSC, the equation:

$$\frac{dX}{dt} = \lim_{t_2 - t_1 \to 0} \frac{a(t_2) - a(t_1)}{A \cdot (t_2 - t_1)} = k(T) \cdot f(x) \tag{3}$$

may be solved directly for k(T).

---

[3]Homer E. Kissinger. "Reaction Kinetics in Differential Thermal Analysis," Analytical Chemistry, Vol. 29, June 1957, p. 1702.

For closely spaced data points, dX/dt is reasonably approximated as $\Delta a/\Delta t \cdot A$. A plot of $\Delta a/A/\Delta t$ versus a/A will indicate the nature of $f(X)$, and k is calculated directly by linear regression analysis for the linear portion of this curve when first order kinetics are observed. One could plot rate versus different algebraic forms of $f(X)$ to see if a straight line results. Again, $f(X)$ would be expected to take the form $(1-X)$ or $X(1-X)$ for explosives.† Figures 6 to 9 are graphic output examples of this program and Tables 1 and 2 provide examples of numeric outputs.

The activation energy is calculated by plotting the values of $k(T)$ obtained at several temperatures versus $1/T$. The slope of this plot is E^*/R.

Previous isothermal kinetic determinations have used the portion of data to the right of the exothermic peak. By integrating Equation 3, a plot of fraction unreacted versus time should have the form:

$$1 - X = \exp\left[-k(T) \cdot t\right] \tag{4}$$

for a first order reaction (Figure 10).[4]

From Equation 1, the ordinate displacement $D(t)$ is given as $\Delta H \cdot k(T) \cdot (1-x)$. For a first order reaction:

$$D(t) = \Delta H \frac{dX}{dt} = \Delta H \cdot k(T) \cdot (1 - x)$$

Substituting Equation 4 for $(1-x)$ gives:

$$D(t) = \Delta H \cdot k(T) \cdot \exp[-k(T) \cdot t]$$

or

$$\ln[D(t)] = \ln[\Delta H \cdot k(T)] - k(T) \cdot t$$

†Jamey and Rodgers. Los Alamos Scientific Laboratory, Private Communication.

[4]Ray N. Rogers. "Differential Scanning Calorimetric Determination of Kinetics Constants of Systems That Melt With Decomposition," Thermochemica ACTA, Vol. 3, 1972, p. 437-447.

Thus a plot of ln D versus time should have slope k(T) for a first order reaction.[5] Figure 11 shows the plot of ln D versus time for RDX Class 5. The linear portion of this curve was used for determination of first order kinetics for $RDX_{(1)} \rightarrow$ Products.

From the form of Equation 1, it is seen that ln D = n ln(1-a) + constants, so a plot of ln D versus ln(1-a) should yield the reaction order n. Figure 12 represents this plot. Calculation of the slope in the region from which kinetic data were calculated gives a value of 1.05, which agrees with the assumption of a first order reaction.

Both the partial area technique and the old technique of plotting ln D versus t give essentially the same answer in the region chosen. The partial area technique is more dynamic in that the fraction of material reacted can be calculated at any point. Thus, if some reaction mechanism is hypothesized, it may be verified with actual experimental numbers.

THERMOGRAVIMETRIC ANALYSIS

While the DSC data are useful for describing the thermodynamics of a system, TGA is necessary for correlating weight loss with temperature. For reactions of the type solid → gas, TGA may be used for kinetic determinations. The fraction X, given as X = M-m/M, M = original mass, and the reaction rate dx/dt may be taken directly from the TGA data.

Numerical analysis for TGA data is the same as that for nonisothermal DSC. Because the temperature rise rate in the TGA instrument is nonlinear, temperature must be calculated after the run is completed. Temperature/mass data are then manually entered into the computer. Temperature is accurately determined by entering millivolt values from strip chart output and converting to temperature values using a standard National Bureau of Standards interpolating polynomial. Data for RDX Class 5 is shown in Table 3 and is plotted in Figures 13 through 15.

This program was developed primarily to investigate the decomposition of rocket motor liners where time, temperature, and mass values are important. If only mass and temperature are needed, the software is easily modified to allow entry of approximately ten times the number of data points. The acquisition of computer compatible thermogravimetric equipment will also allow acquisition of more data points when all three reference points are required.

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[5]Ray N. Rogers. "Simplified Determination of Rate Constants by Scanning Calorimetry", Analytical Chemistry, Vol. 44, December 1971, p. 1336.

CONCLUSIONS

The acquisition and analysis of large amounts of data with a digital computer has opened a new field in the area of thermal analysis. Plotting and numerical analysis software allow the data to be reduced in a fraction of the time previously needed and permit use of a larger number of data points.

In addition, fast integrating algorithms allow use of partial area techniques which will prove to be very influential in future analytical procedures.

The successful application of these computer techniques in the determination of isothermal kinetics should prove extremely useful in determining the cook-off hazards from aging studies and understanding cook-off behavior.

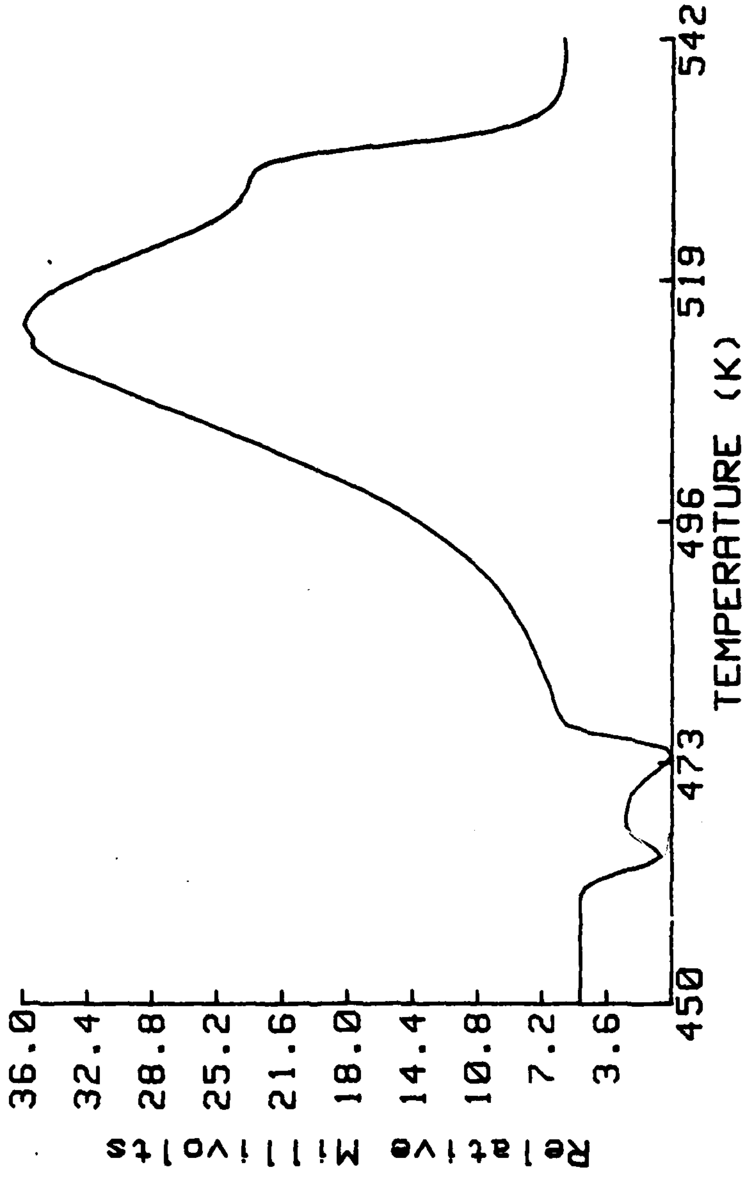

FIGURE 1. DSC Plot of RDX Class 5. (Scanning Rate is 10 deg/min.)

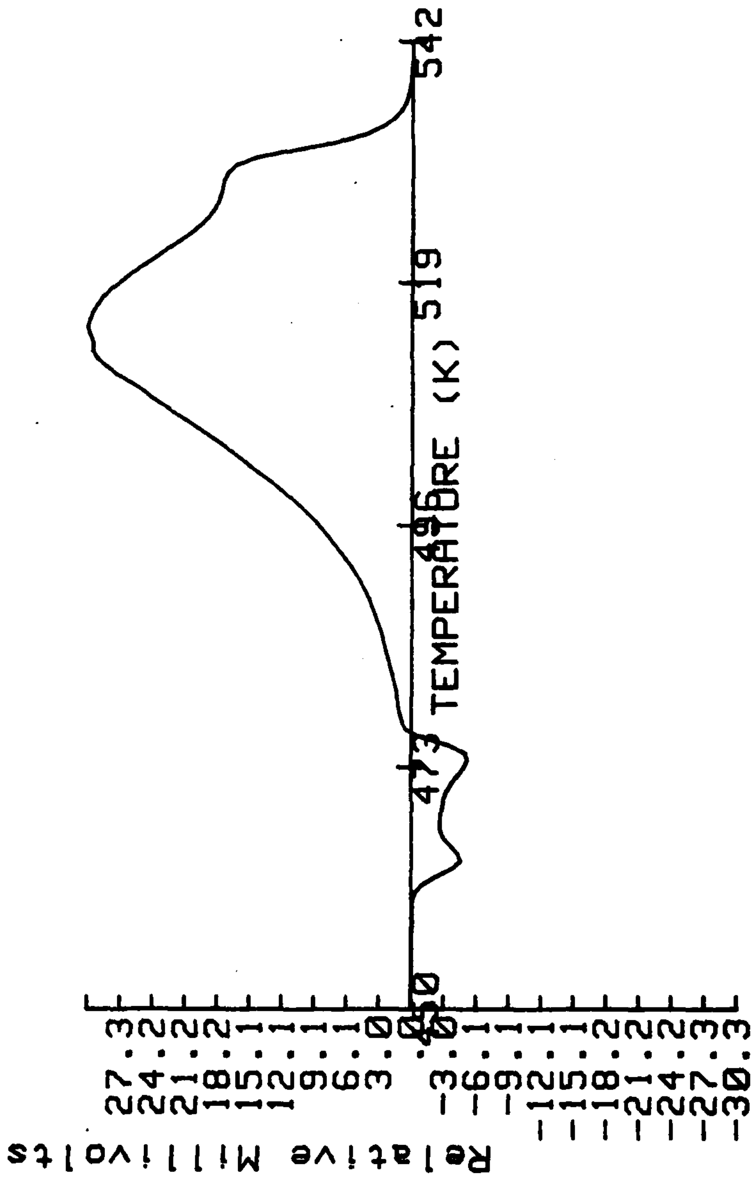

FIGURE 2. Plot of RDX Class 5 with a Linear Baseline Correction.

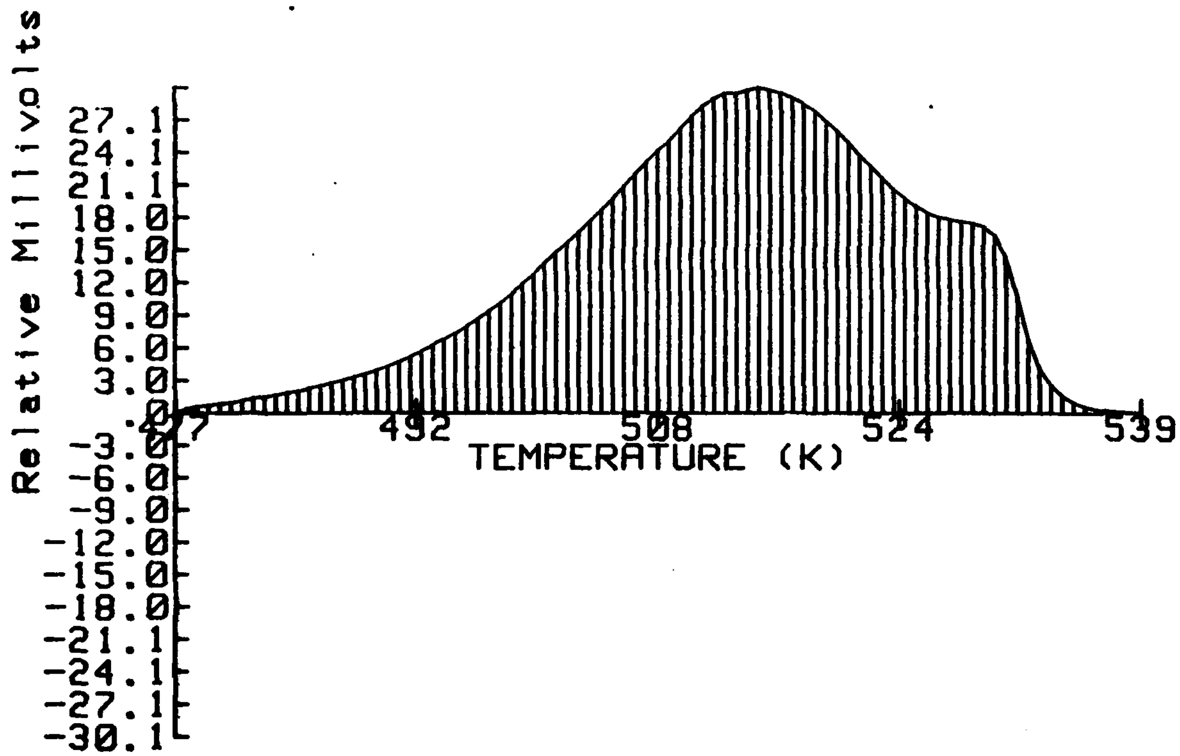

FIGURE 3. Plot of RDX Class 5. (Shaded region denotes area calculated by the computer. Ratios of partial areas to total area gives fraction reacted. The actual value of energy released may be obtained by comparison with a primary standard.)

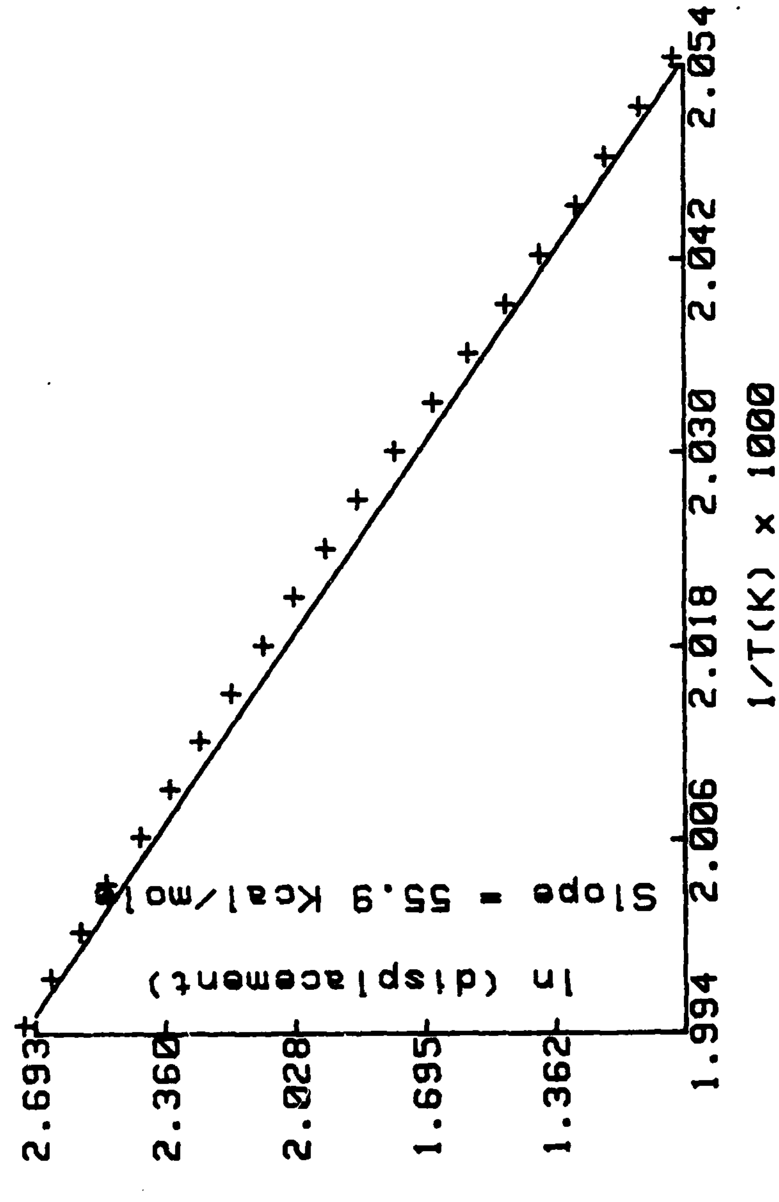

FIGURE 4. Plot of ln D vs 1/T to Determine Activation Energy E^*.

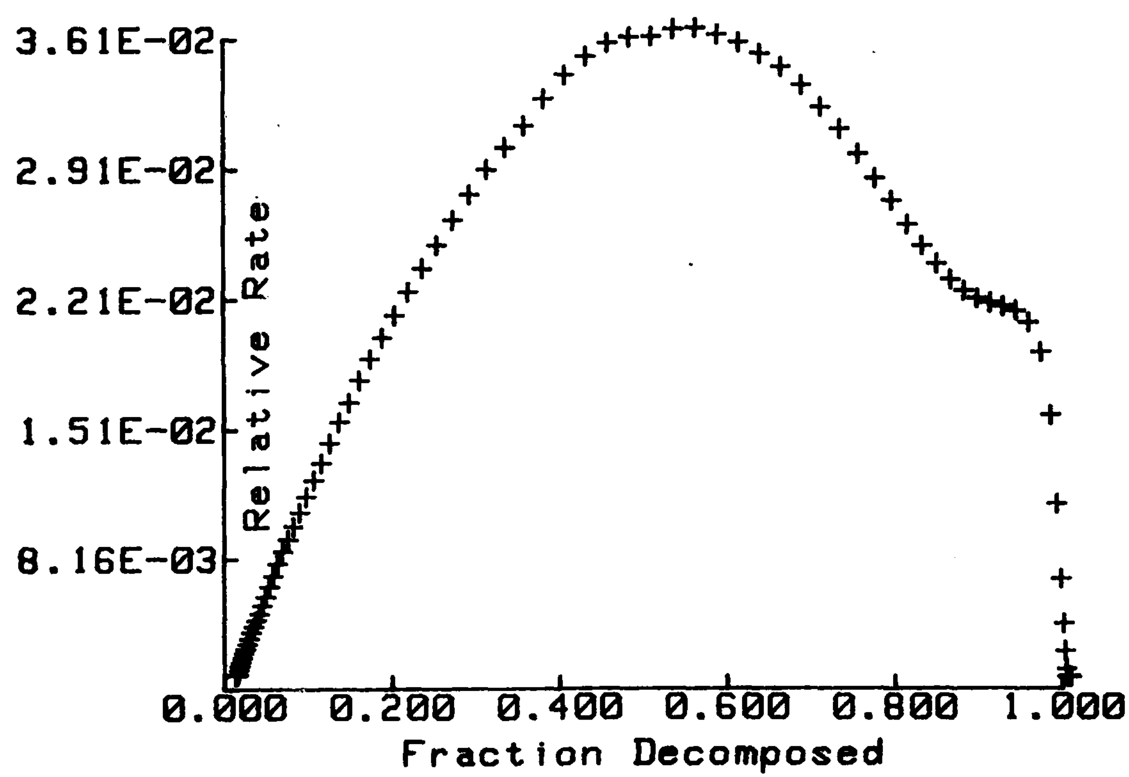

FIGURE 5. Kinetic Plot of RDX Class 5 at 10 deg/min.

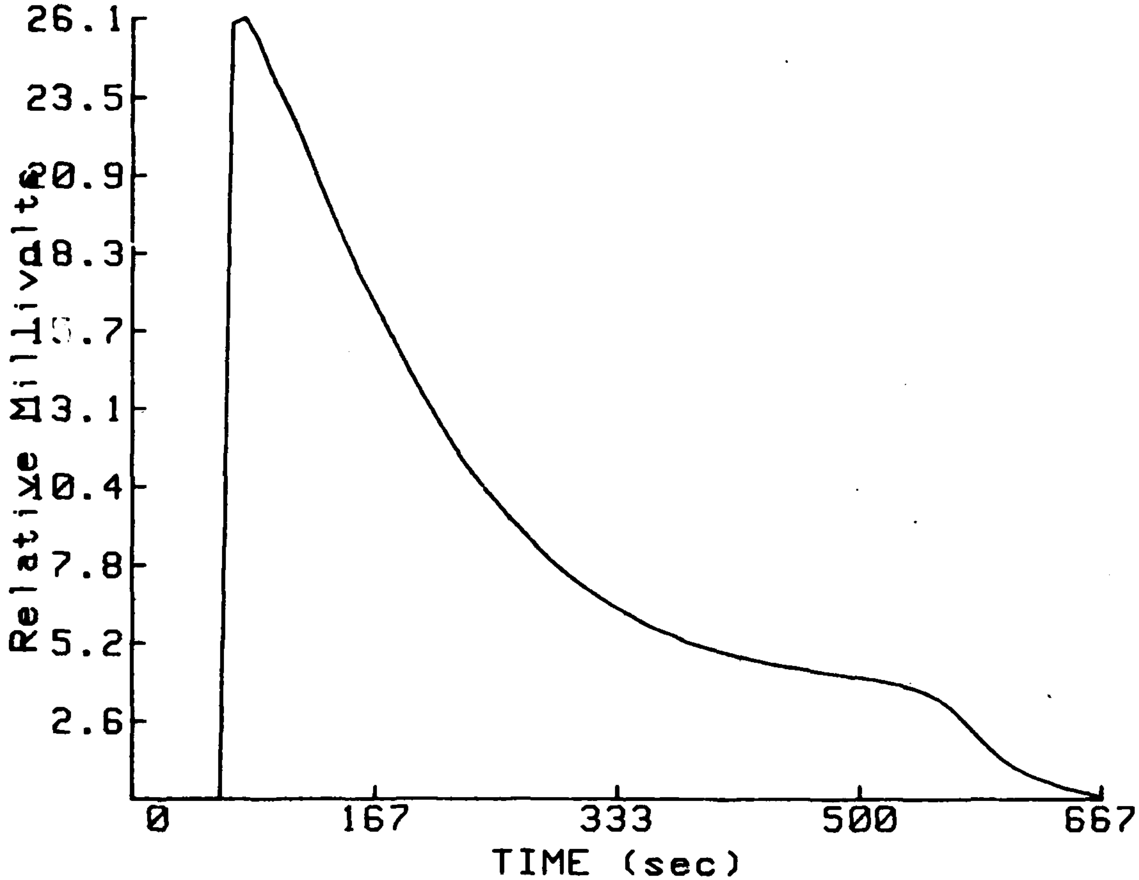

FIGURE 6. Isothermal Run of RDX Class 5 on Perkin Elmer DSC II. (Temperature is 504 K.)

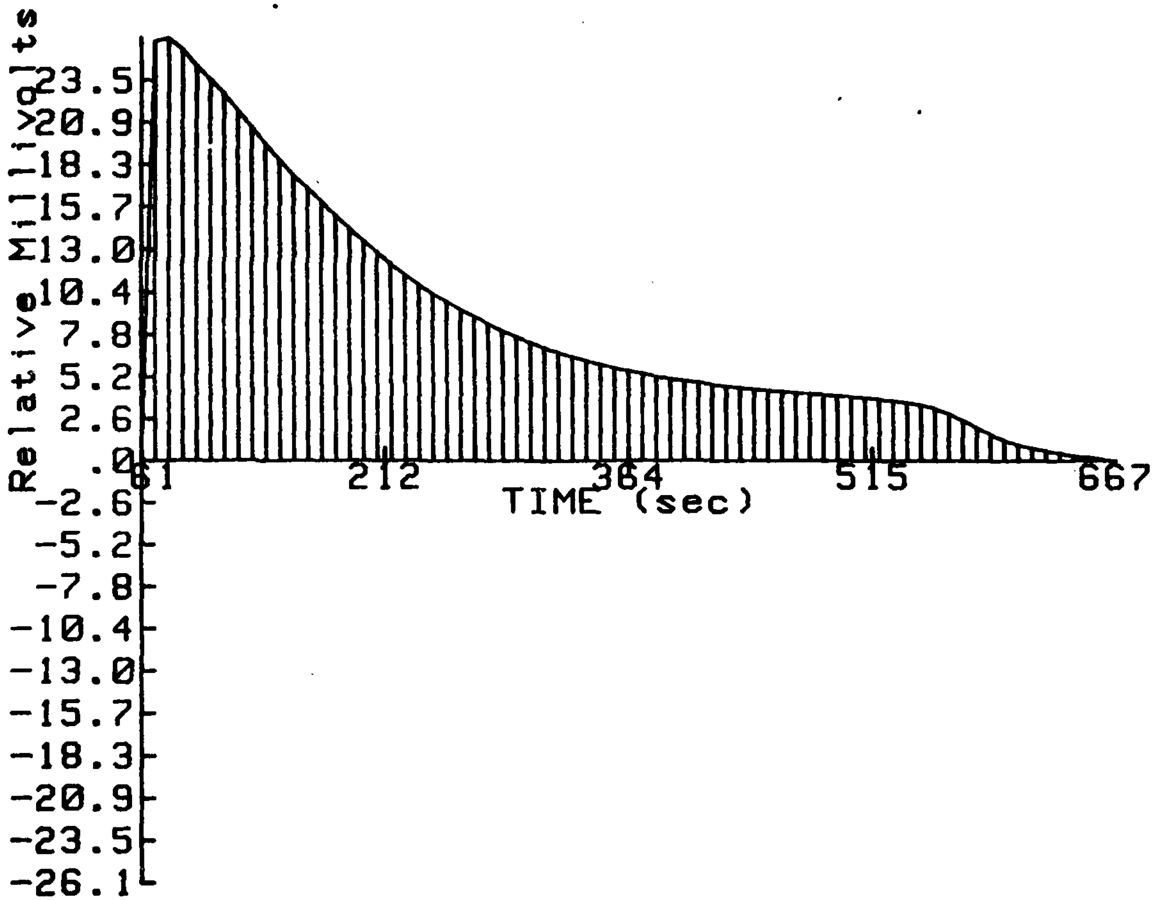

FIGURE 7. Isothermal Run of RDX Class 5 on Perkin Elmer DSC II. (The shaded area represents the area calculated by the computer. Endpoints for the determination as well as points used for baseline determination are operator selectable.)

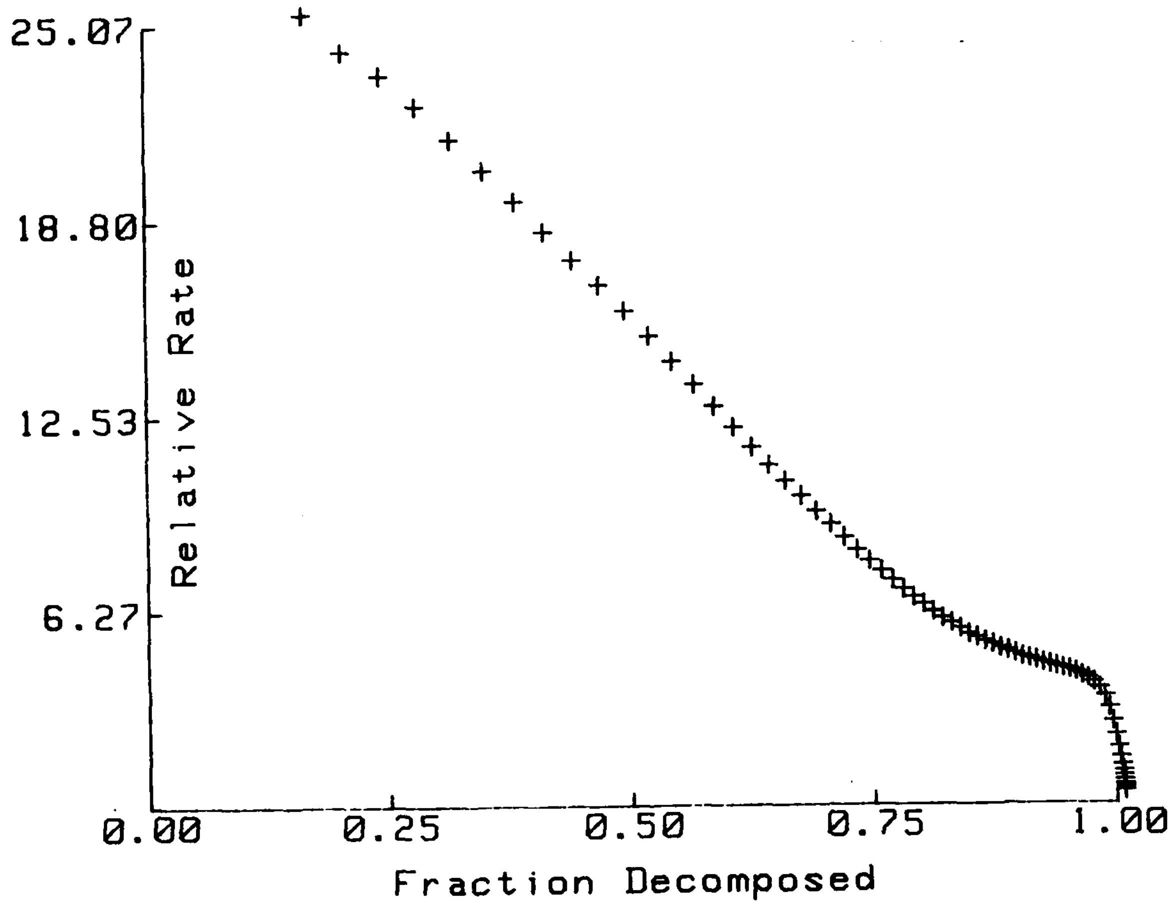

FIGURE 8. Plot of the Rate of Change of the Area Fraction vs the Area Fraction. (The linear portion of the curve is chosen for the determination of kinetic parameters.)

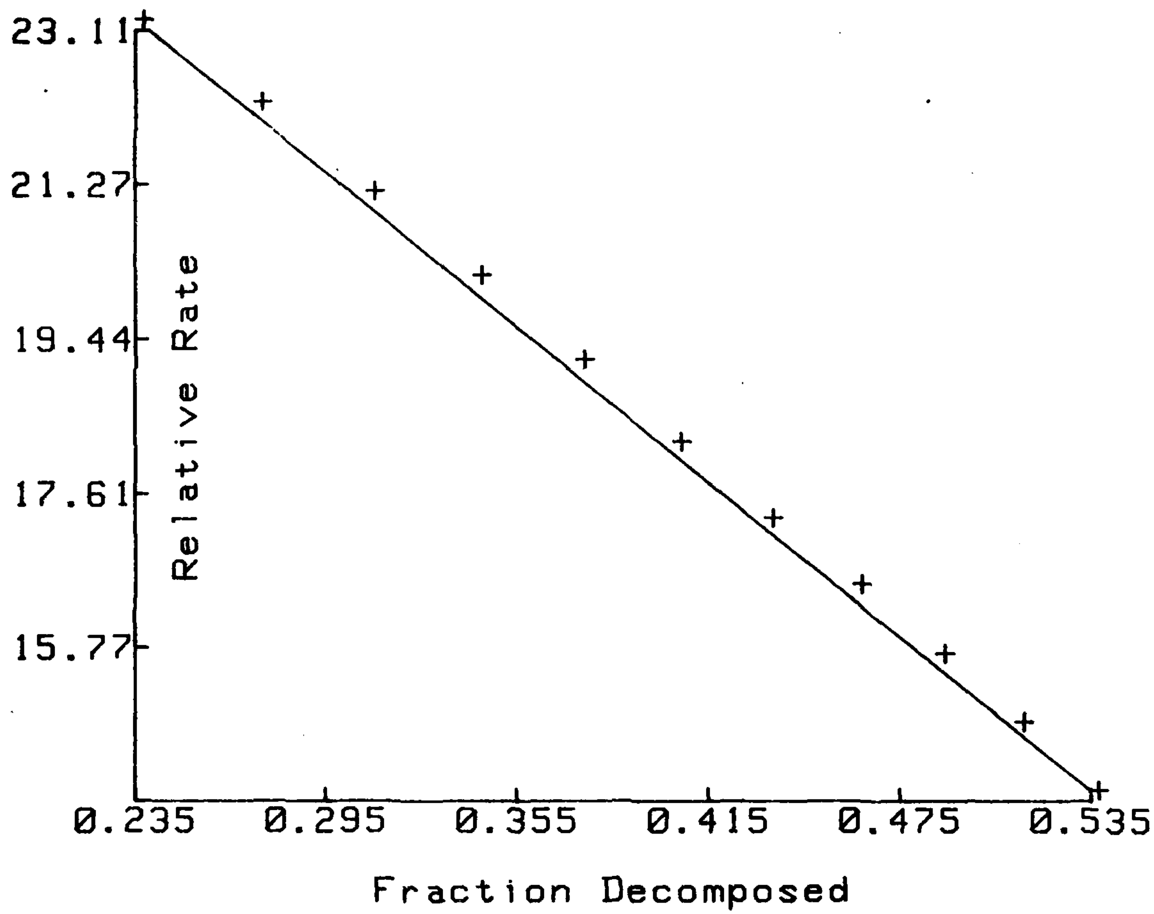

FIGURE 9. Graphics of Linear Regression Analysis of Linear Portion of Curve in Figure 8. (The calculated slope is 30.6 +/- .2 sec^{-1}. Dividing this by the total area (Table 2) yields a rate constant of 0.00595 +/- 0.00004 sec^{-1}.)

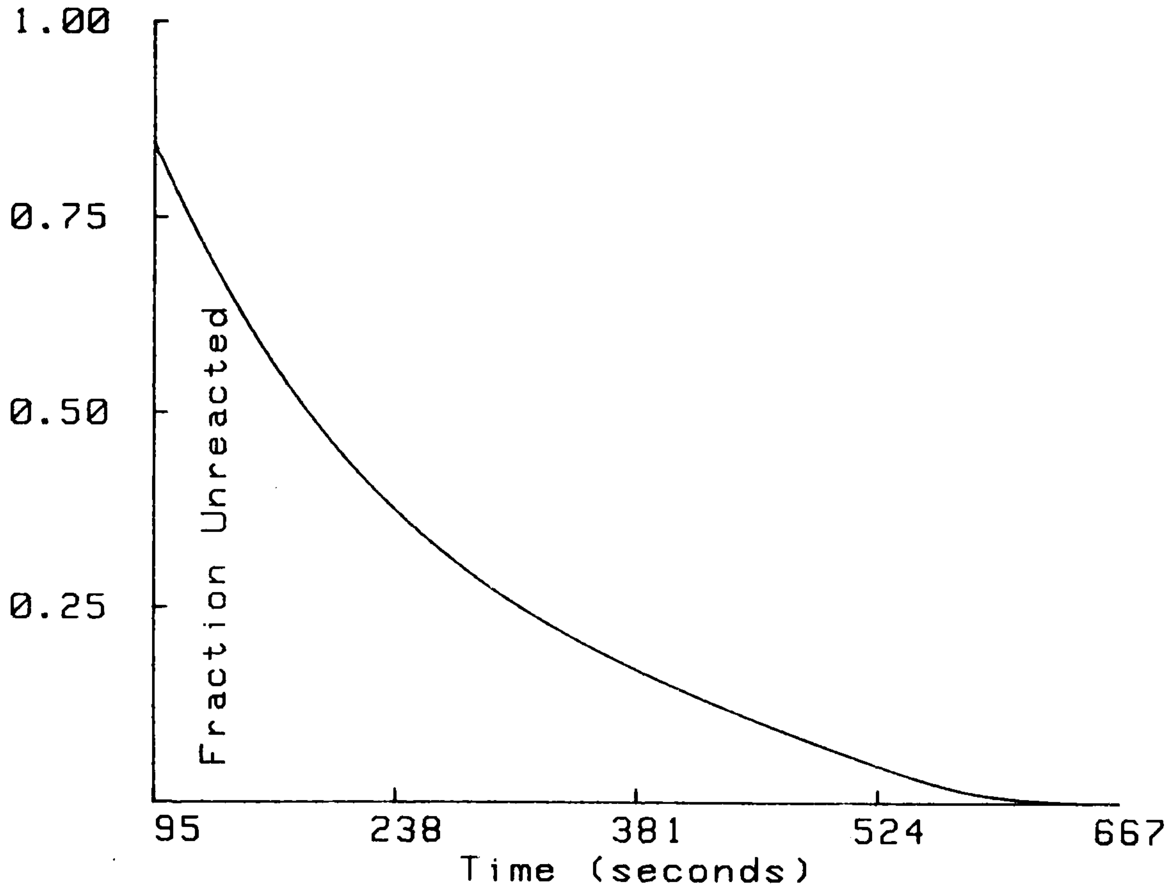

FIGURE 10. A Plot of Fraction Unreacted (1-x) vs Time for RDX Class 5. (The plot has the shape expected from theory for a first order reaction.)

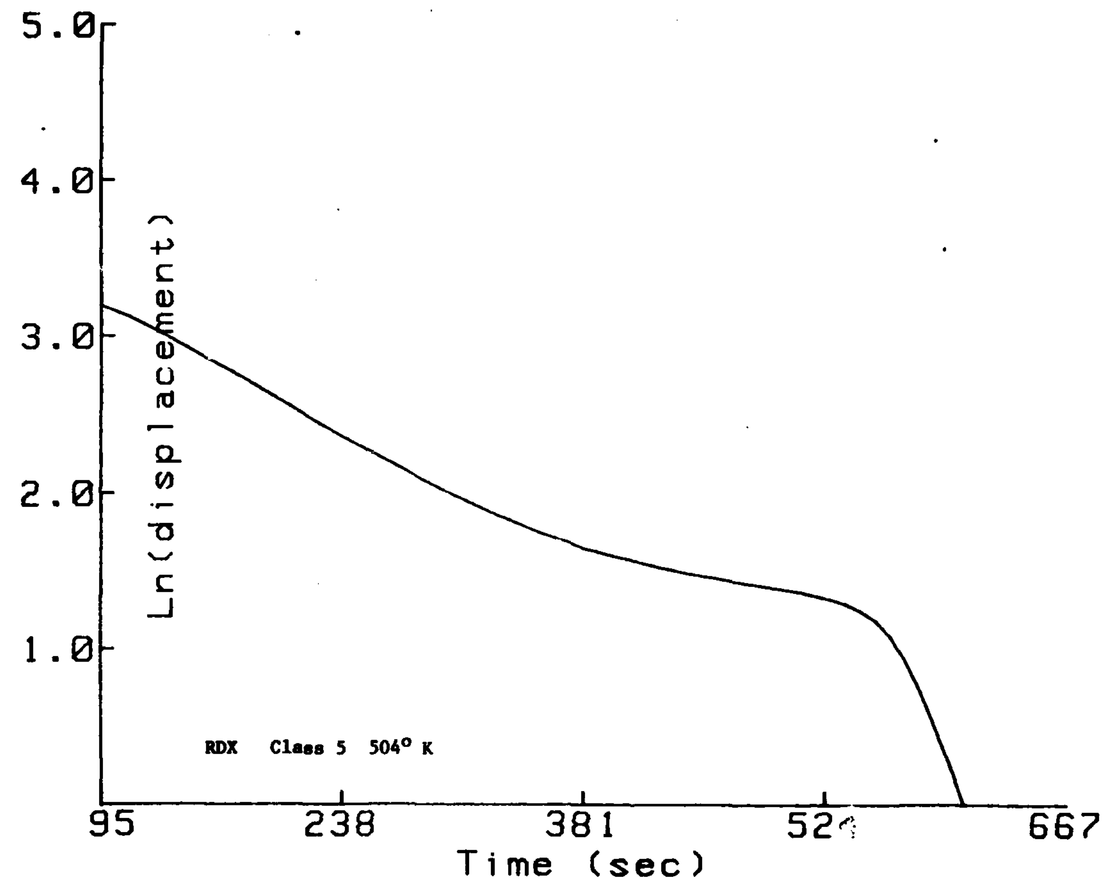

FIGURE 11. Plot of ln D Vs Time. (The slope of the linear portion was calculated to be 0.00604 sec^{-1}. This is in excellent agreement with the rate constant calculated in Figure 9.)

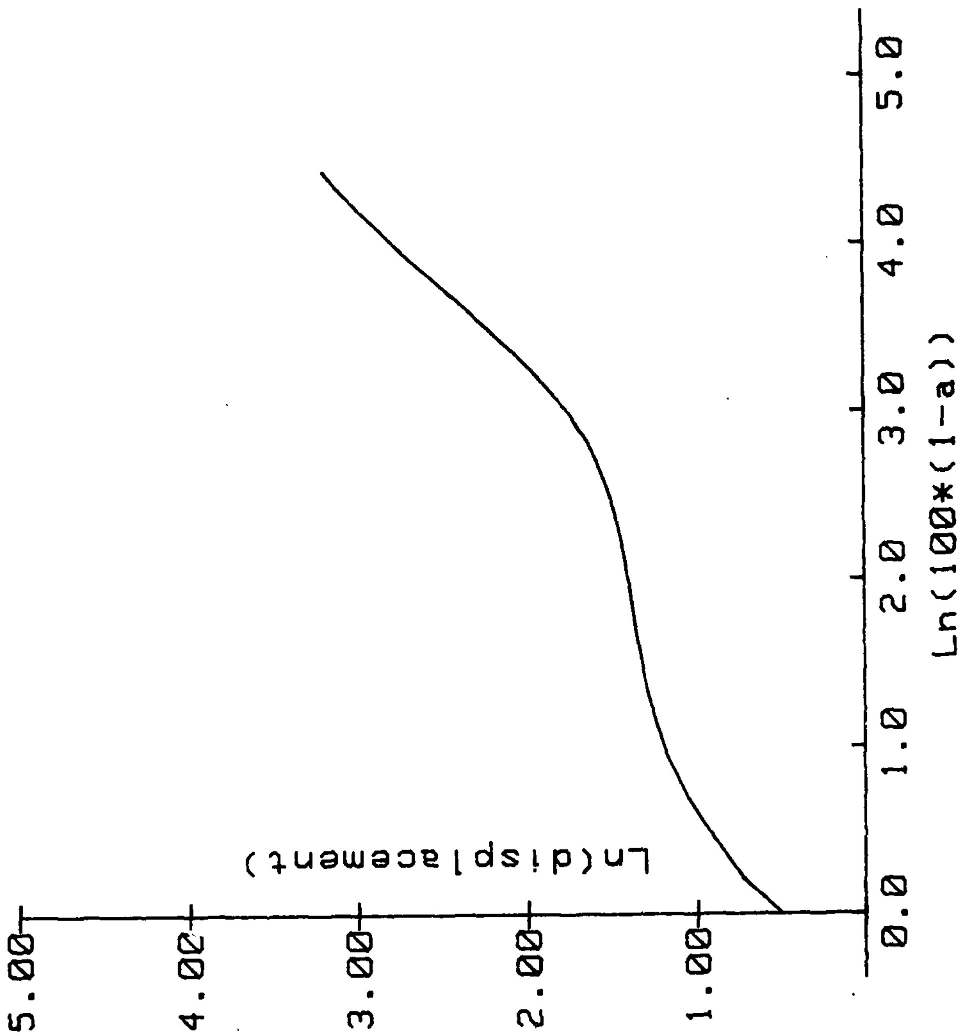

FIGURE 12. "Order" Plot for RDX Class 5. (Slope of linear portion is 1.05 +/- 0.01.)

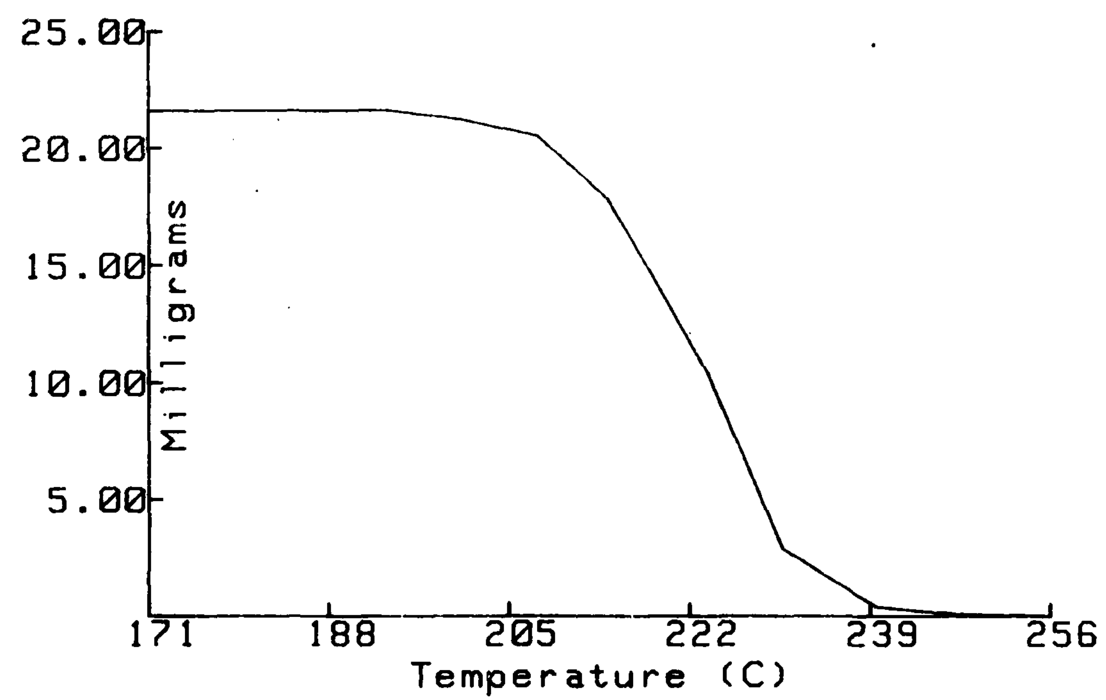

FIGURE 13. Graphics of Thermogravimetric Analysis of RDX Class 5. (Scan rate is 3 deg/min.)

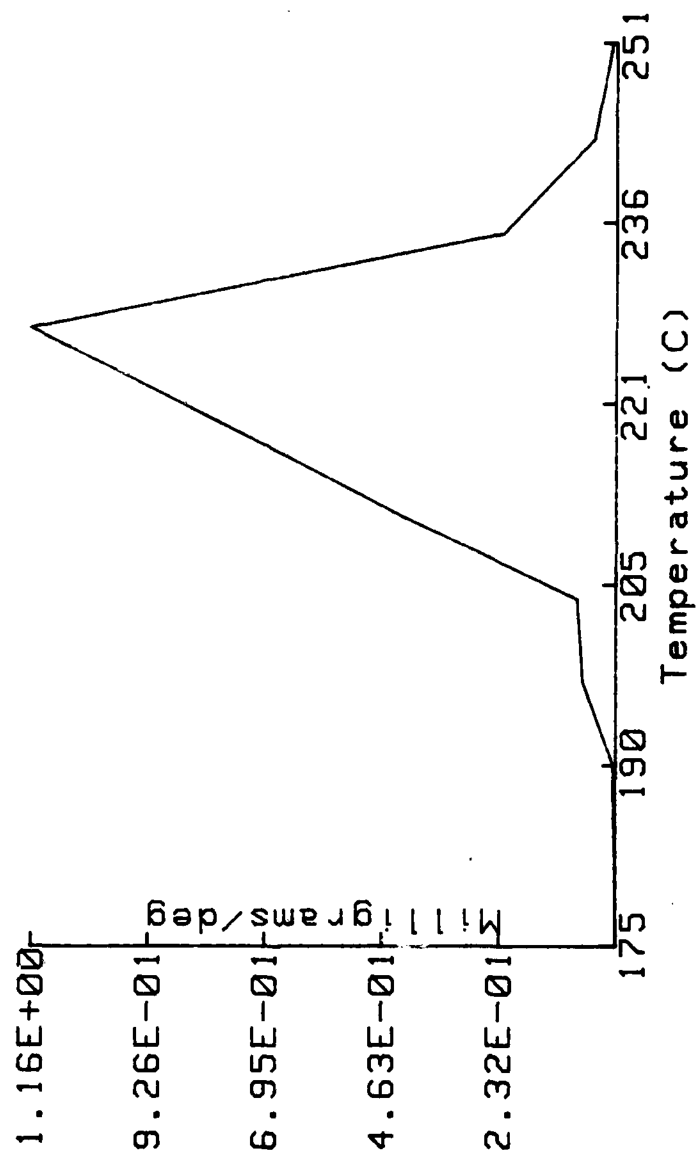

FIGURE 14. Computer-Generated Plot of the Derivative of the TGA Curve in Figure 13.

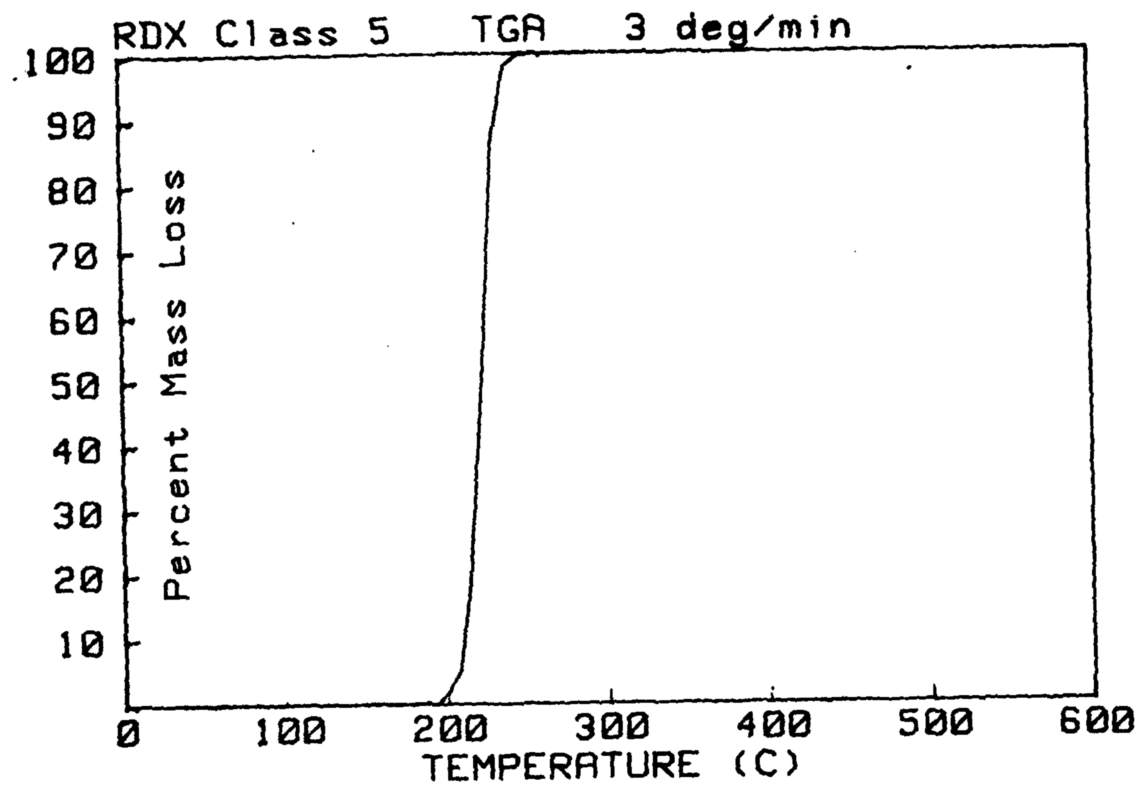

FIGURE 15. Graphics of TGA Plot of Figure 13 Showing % Mass Lost. (For gaseous products, this indicates fraction reacted. This type of plot is useful when comparing different materials.)

TABLE 1. Computer Printout of Data Used to Determine Kinetic Parameters. (The section of the data that is used for the calculations is operator selectable.)

RDX Class 5   10 deg/min   2 mcal/sec   2.32 mg
October 2, 1981
Kinetics determination

Temp(K)	1/T	Area Fract.	LN(ordinate)	Relative Rate	Pt#
479	2.09E-03	0.004	.001	1.30E-03	5
480	2.08E-03	0.005	.001	1.30E-03	6
481	2.08E-03	0.006	.126	1.36E-03	7
482	2.08E-03	0.007	.283	1.57E-03	8
482	2.07E-03	0.008	.415	1.80E-03	9
483	2.07E-03	0.010	.525	2.02E-03	10
484	2.07E-03	0.011	.646	2.24E-03	11
485	2.06E-03	0.013	.734	2.49E-03	12
485	2.06E-03	0.015	.830	2.71E-03	13
486	2.06E-03	0.017	.923	2.97E-03	14
487	2.05E-03	0.020	1.029	3.27E-03	15
487	2.05E-03	0.022	1.117	3.60E-03	16
488	2.05E-03	0.025	1.203	3.91E-03	17
489	2.05E-03	0.028	1.279	4.24E-03	18
490	2.04E-03	0.032	1.372	4.59E-03	19
490	2.04E-03	0.035	1.461	5.03E-03	20
491	2.04E-03	0.039	1.557	5.50E-03	21
492	2.03E-03	0.044	1.647	6.04E-03	22
493	2.03E-03	0.049	1.745	6.61E-03	23
493	2.03E-03	0.054	1.840	7.28E-03	24
494	2.02E-03	0.060	1.922	7.95E-03	25
495	2.02E-03	0.066	2.001	8.60E-03	26
496	2.02E-03	0.073	2.080	9.31E-03	27
496	2.01E-03	0.080	2.161	1.01E-02	28
497	2.01E-03	0.088	2.242	1.09E-02	29
498	2.01E-03	0.097	2.318	1.18E-02	30
498	2.01E-03	0.106	2.395	1.27E-02	31
499	2.00E-03	0.116	2.481	1.38E-02	32
500	2.00E-03	0.127	2.549	1.49E-02	33
501	2.00E-03	0.139	2.624	1.60E-02	34
501	1.99E-03	0.152	2.693	1.72E-02	35
502	1.99E-03	0.165	2.754	1.83E-02	36
503	1.99E-03	0.179	2.814	1.95E-02	37
504	1.99E-03	0.194	2.874	2.07E-02	38
504	1.98E-03	0.210	2.932	2.19E-02	39
505	1.98E-03	0.227	2.986	2.32E-02	40
506	1.98E-03	0.245	3.039	2.44E-02	41
507	1.97E-03	0.264	3.092	2.58E-02	42
507	1.97E-03	0.284	3.142	2.71E-02	43
508	1.97E-03	0.305	3.188	2.85E-02	44
509	1.97E-03	0.327	3.223	2.97E-02	45
509	1.96E-03	0.349	3.269	3.08E-02	46
510	1.96E-03	0.373	3.312	3.23E-02	47
511	1.96E-03	0.398	3.347	3.36E-02	48
512	1.95E-03	0.423	3.372	3.46E-02	49
512	1.95E-03	0.449	3.388	3.53E-02	50
513	1.95E-03	0.475	3.387	3.56E-02	51
514	1.95E-03	0.501	3.397	3.56E-02	52
515	1.94E-03	0.527	3.405	3.60E-02	53
515	1.94E-03	0.554	3.399	3.61E-02	54
516	1.94E-03	0.580	3.389	3.58E-02	55
517	1.94E-03	0.606	3.374	3.53E-02	56
518	1.93E-03	0.631	3.356	3.47E-02	57
518	1.93E-03	0.656	3.332	3.40E-02	58
519	1.93E-03	0.660	3.296	3.30E-02	59

TABLE 1. (Contd.)

520	1.92E-03	0.704	3.261	3.13E-02	60
520	1.92E-03	0.726	3.220	3.07E-02	61
521	1.92E-03	0.746	3.173	2.93E-02	62
522	1.92E-03	0.768	3.130	2.80E-02	63
523	1.91E-03	0.788	3.083	2.68E-02	64
523	1.91E-03	0.806	3.034	2.56E-02	65
524	1.91E-03	0.824	2.992	2.44E-02	66
525	1.91E-03	0.841	2.952	2.34E-02	67
526	1.90E-03	0.858	2.921	2.26E-02	68
526	1.90E-03	0.874	2.899	2.20E-02	69
527	1.90E-03	0.890	2.885	2.16E-02	70
528	1.89E-03	0.906	2.875	2.14E-02	71
529	1.89E-03	0.921	2.867	2.12E-02	72
529	1.89E-03	0.936	2.849	2.09E-02	73
530	1.89E-03	0.951	2.803	2.03E-02	74
531	1.88E-03	0.965	2.673	1.87E-02	75
531	1.88E-03	0.976	2.376	1.53E-02	76
532	1.88E-03	0.984	1.920	1.05E-02	77
533	1.88E-03	0.989	1.443	6.47E-03	78
534	1.87E-03	0.992	.990	4.07E-03	79
534	1.87E-03	0.994	.515	2.58E-03	80
535	1.87E-03	0.995	.052	1.60E-03	81
536	1.87E-03	0.996	.001	1.18E-03	82
537	1.86E-03	0.996	.001	1.22E-03	83
537	1.86E-03	0.997	.001	1.20E-03	84
538	1.86E-03	0.998	.001	1.20E-03	85
539	1.86E-03	0.999	.001	1.20E-03	96
539	1.85E-03	1.000	.001	1.20E-03	87

TABLE 2. Computer Printout of Data Used for Graphics and Kinetic Parameter Calculations.

TIME s	AREA	FRACT A	AREA INCREMENT	RATE OF INCREASE	Fr#
95	800	0.156	216.982	25.067	5
104	1007	0.196	206.605	23.863	6
113	1207	0.235	200.003	23.106	7
121	1398	0.272	191.548	22.124	8
130	1581	0.307	182.245	21.057	9
139	1754	0.341	173.670	20.059	10
147	1919	0.373	164.955	19.061	11
156	2076	0.404	156.694	18.094	12
165	2225	0.432	148.803	17.191	13
173	2367	0.460	142.030	16.403	14
182	2502	0.486	134.618	15.572	15
191	2629	0.511	127.725	14.754	16
199	2750	0.535	120.645	13.939	17
208	2864	0.557	114.329	13.202	18
217	2973	0.578	108.207	12.499	19
225	3075	0.598	102.329	11.819	20
234	3172	0.616	96.785	11.183	21
242	3264	0.634	91.899	10.614	22
251	3351	0.651	87.456	10.100	23
260	3434	0.668	83.277	9.617	24
268	3513	0.683	78.980	9.123	25
277	3589	0.698	75.347	8.702	26
286	3660	0.711	71.571	8.269	27
294	3728	0.725	68.069	7.861	28
303	3793	0.737	65.031	7.512	29
312	3856	0.749	62.191	7.183	30
320	3915	0.761	59.541	6.877	31
329	3972	0.772	57.043	6.587	32
338	4027	0.783	54.783	6.329	33
346	4080	0.793	52.794	6.099	34
355	4130	0.803	50.711	5.856	35
364	4179	0.812	48.898	5.646	36
372	4227	0.822	47.532	5.491	37
381	4273	0.831	45.991	5.313	38
390	4317	0.839	44.415	5.129	39
398	4361	0.848	43.472	5.021	40
407	4402	0.856	42.417	4.897	41
416	4445	0.864	41.502	4.795	42
424	4485	0.872	40.514	4.678	43
433	4525	0.879	39.628	4.577	44
442	4564	0.887	38.837	4.486	45
450	4602	0.894	38.068	4.395	46
459	4639	0.902	37.564	4.338	47
468	4676	0.909	36.961	4.269	48
476	4712	0.916	36.286	4.191	49
485	4748	0.923	35.751	4.129	50
494	4784	0.930	35.279	4.074	51
502	4818	0.937	34.702	4.008	52
511	4852	0.943	34.209	3.951	53
520	4886	0.950	33.559	3.876	54
528	4919	0.956	32.772	3.786	55
537	4951	0.962	31.952	3.690	56
546	4982	0.968	30.791	3.556	57
554	5011	0.974	29.172	3.368	58
563	5038	0.979	26.901	3.107	59
571	5061	0.984	23.672	2.734	60
580	5081	0.988	19.826	2.290	61
589	5097	0.991	16.030	1.853	62
597	5110	0.993	12.610	1.457	63
606	5120	0.995	9.803	1.132	64
615	5127	0.997	7.634	0.882	65
623	5133	0.998	5.936	0.686	66
632	5139	0.999	4.587	0.530	67
641	5141	0.999	3.329	0.385	68
649	5143	1.000	2.106	0.243	69
658	5144	1.000	1.339	0.155	70
667	5145	1.000	0.346	0.040	71

TABLE 2. (Contd.)

Pt#	Time(sec)	Y	Log(Y)	a	(1-a)	Ln 100*(1-a
5	95	24.4	3.193	0.156	0.844	4.436
6	104	23.5	3.158	0.196	0.804	4.387
7	113	22.6	3.120	0.235	0.765	4.338
8	121	21.6	3.071	0.272	0.728	4.288
9	130	20.6	3.023	0.307	0.693	4.238
10	139	19.6	2.973	0.341	0.659	4.188
11	147	18.6	2.922	0.373	0.627	4.138
12	156	17.6	2.868	0.404	0.596	4.088
13	165	16.8	2.822	0.432	0.568	4.039
14	173	16.0	2.771	0.460	0.540	3.989
15	182	15.2	2.719	0.486	0.514	3.939
16	191	14.3	2.662	0.511	0.489	3.890
17	199	13.6	2.607	0.535	0.465	3.840
18	208	12.8	2.553	0.557	0.443	3.792
19	217	12.2	2.498	0.578	0.422	3.743
20	225	11.5	2.441	0.598	0.402	3.695
21	234	10.9	2.388	0.616	0.384	3.647
22	242	10.3	2.336	0.634	0.366	3.599
23	251	9.9	2.289	0.651	0.349	3.551
24	260	9.4	2.236	0.668	0.332	3.504
25	268	8.9	2.188	0.683	0.317	3.457
26	277	8.5	2.138	0.698	0.302	3.409
27	286	8.1	2.096	0.711	0.289	3.362
28	294	7.7	2.039	0.725	0.275	3.315
29	303	7.3	1.994	0.737	0.263	3.268
30	312	7.0	1.950	0.749	0.251	3.221
31	320	6.7	1.906	0.761	0.239	3.174
32	329	6.4	1.864	0.772	0.228	3.126
33	338	6.2	1.827	0.783	0.217	3.079
34	346	6.0	1.788	0.793	0.207	3.030
35	355	5.7	1.747	0.803	0.197	2.981
36	364	5.6	1.717	0.812	0.188	2.932
37	372	5.4	1.689	0.822	0.178	2.882
38	381	5.2	1.649	0.831	0.169	2.830
39	390	5.1	1.626	0.839	0.161	2.778
40	398	5.0	1.600	0.848	0.152	2.724
41	407	4.8	1.579	0.856	0.144	2.668
42	416	4.7	1.555	0.864	0.136	2.611
43	424	4.6	1.531	0.872	0.128	2.551
44	433	4.5	1.512	0.879	0.121	2.489
45	442	4.4	1.489	0.887	0.113	2.425
46	450	4.4	1.474	0.894	0.106	2.357
47	459	4.3	1.460	0.902	0.098	2.285
48	468	4.2	1.442	0.909	0.091	2.209
49	476	4.2	1.425	0.916	0.084	2.129
50	485	4.1	1.412	0.923	0.077	2.042
51	494	4.0	1.396	0.930	0.070	1.949
52	502	4.0	1.382	0.937	0.063	1.848
53	511	3.9	1.365	0.943	0.057	1.737
54	520	3.8	1.343	0.950	0.050	1.616
55	528	3.7	1.320	0.956	0.044	1.480
56	537	3.6	1.290	0.962	0.038	1.328
57	546	3.5	1.244	0.968	0.032	1.155
58	554	3.3	1.181	0.974	0.026	0.950
59	563	2.9	1.078	0.979	0.021	0.734
60	571	2.5	0.922	0.984	0.016	0.485
61	580	2.1	0.726	0.988	0.012	0.214
62	589	1.6	0.497	0.991	0.009	-0.076
63	597	1.3	0.248	0.993	0.007	-0.383
64	606	1.0	-0.003	0.995	0.005	-0.711
65	615	.8	-0.253	0.997	0.003	-1.070
66	623	.6	-0.508	0.998	0.002	-1.480
67	632	.5	-0.768	0.999	0.001	-1.970
68	641	.3	-1.215	0.999	0.001	-2.600
69	649	.2	-1.567	1.000	0.000	-3.419
70	658	.1	-2.416	1.000	0.000	-5.003

TABLE 3. Computer Printout of Time, Temperature, Mass Loss Data for TGA Program.

RDX Class 5 TGA 3 deg/min.
Initial mass is 21.59 mg. Heating rate is 3 deg/min
Sensitivity is 10 mg/mv

Temperature (C)	Time(min)	Mass(mg)	% Mass Loss	Data Pt #
36	0.00	21.6	0.00	1
37	2.50	21.6	0.00	2
38	5.00	21.6	0.00	3
41	7.50	21.6	0.00	4
45	10.00	21.6	0.00	5
49	12.50	21.6	0.00	6
55	15.00	21.6	0.00	7
61	17.50	21.6	0.00	8
67	20.00	21.6	0.00	9
74	22.50	21.6	0.00	10
82	25.00	21.6	0.00	11
90	27.50	21.6	0.00	12
99	30.00	21.6	0.00	13
108	32.50	21.6	0.00	14
117	35.00	21.6	0.00	15
126	37.50	21.6	0.00	16
134	40.00	21.6	0.00	17
142	42.50	21.6	0.00	18
149	45.00	21.6	0.00	19
157	47.50	21.6	0.00	20
164	50.00	21.6	0.00	21
171	52.50	21.6	0.00	22
179	55.00	21.6	0.00	23
187	57.50	21.6	0.00	24
194	60.00	21.6	0.00	25
201	62.50	21.2	1.85	26
208	65.00	20.5	5.09	27
214	67.50	17.8	17.60	28
224	70.00	10.4	51.88	29
231	72.50	2.9	86.61	30
239	75.00	.4	98.19	31
246	77.50	.1	99.58	32
256	80.00	0.0	100.00	33
264	82.50	0.0	100.00	34
272	85.00	0.0	100.00	35
281	87.50	0.0	100.00	36
291	90.00	0.0	100.00	37

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APPENDIX A

Program for Acquisition and Analysis of Constant Heating Rate Differential Scanning Calorimeter Data

PROGRAM FOR AQUISITION AND ANALYSIS OF THERMOGRAVIMETRIC DATA

```
10    OPTION BASE 1
20    COM T(300),Mass(300),Mass1(300),Time(300),N,M0,A$[80],B$[80]
25    COM A(300),B(300),Anew(300),Bnew(300),Deriv(300)
30    COM Aa(0:9) ! Coefficients for interpolating polynomial
40    MAT READ Aa! for type S thermocouple.
45    LINPUT "ENTER RUN IDENTIFIER",B$
50    Plot=1
60    IF Plot>1 THEN LINPUT "DO YOU WANT TO PLOT ANOTHER RUN?",Cont$
62    IF (Plot>1) AND (Cont$[1,1]<>"Y") THEN GOSUB Continue
65    INPUT "ENTER NUMBER OF DATA POINTS",N
70    REDIM T(N),Mass(N),Mass1(N),Time(N)
80    INPUT "ENTER MILLIVOLT READING FOR INDIUM MELT",Mp
90    INPUT "ENTER THERMOCOUPLE GAIN (1 OR 5)",Gain
100   INPUT "ENTER INITIAL MASS",M0
105   INPUT "ENTER HEATING RATE",Hrate
110   INPUT "ENTER MILLIVOLT VALUE FOR INITIAL MASS",Mv
115   INPUT "ENTER MASS SENSITIVITY (mg/mv): 1 or 10 ",Sens
120   PRINTER IS 16
130   FOR I=1 TO N
140   PRINT LIN(6)
150   PRINT USING 220;I
160   INPUT X,Y
170   X=(X-Mp)/Gain+1.082 ! Calculate S thermocouple output.
180   T(I)=FNScal(X/1000)  ! Calculate Temperature.
190   Mass(I)=M0+Sens*(Y-Mv)  ! Calculate Mass For (Sens)mg/mv sensitivity.
195   Time(I)=(I-1)*2.5  ! Time in minutes: 5 min/inch chart speed.
200   Mass1(I)=(M0-Mass(I))/M0*100 !Percent Mass Loss.
202   PRINT PAGE
205   PRINT USING 225;T(I),Mass(I),Time(I)
210   NEXT I
220   IMAGE "ENTER MILLIVOLT READINGS FOR POINT #",DD,"  (Temp.,Mass)"
225   IMAGE "Temperature is ",DDD," C;   Mass is ",DD.DD," mg.;   Time is ",DDDD
.D," min."
230   GOSUB Printer
235   LINPUT "DO YOU WANT THE DATA STORED?",Store$
236   IF Store$[1,1]="Y" THEN CALL Store(T(*),Mass(*),M0,N,B$)
240   IF Plot>1 THEN GOSUB S
245   REM  Plot % Mass loss vs Temperature
250   INPUT "ENTER PLOTTER CODE:  1=CRT; 2=9872A",Plotter
260   IF Plotter=1 THEN PLOTTER IS "GRAPHICS"
270   IF Plotter=2 THEN PLOTTER IS 7,5,"9872A"
280   GRAPHICS
290   LOCATE 15,90,20,70
295   INPUT "ENTER HIGHEST PERCENTAGE DESIRED ON PLOT",Q
300   SCALE 0,600,0,Q
310   LINPUT "ENTER PLOT LABEL",A$
320   Xname$="TEMPERATURE (C)"
330   Yname$="Percent Mass Loss"
340   AXES 100,Q/10,0,0
350   FRAME
360   MOVE T(1),Mass1(1)
370   FOR I=2 TO N  !PLOT FIRST ARRAY.
380   DRAW T(I),Mass1(I)
390   NEXT I
400   PENUP
410   LORG 6  ! Label X Axis
420   FOR I=0 TO 600 STEP 100
```

```
430   MOVE I,-2
440   LABEL I
450   NEXT I
460   LORG 8 !Label Y Axis
470   FOR I=Q/10 TO Q STEP Q/10
480   MOVE 0,I
490   LABEL I
500   NEXT I
510   LORG 1  ! Label Plot.
520   MOVE 0,1.02*Q
530   LABEL A$
540   LORG 6
541   MOVE 300,-.08*Q
542   LABEL Xname$
543   MOVE 25,Q/2
544   LDIR PI/2
545   LABEL Yname$
547   PENUP
548   LDIR 0
550   PAUSE
553   IF Plotter=1 THEN DUMP GRAPHICS
555   LINPUT "WOULD YOU LIKE TO REPEAT THIS PLOT?",Rpt$
560   IF Rpt$[1,1]="Y" THEN GOTO 250
565   Plot=Plot+1
569   GOTO 60
570 S:   ! Plot other arrays
580   IF Plot=2 THEN LINE TYPE 4
590   IF Plot=3 THEN LINE TYPE 6
600   IF Plot=4 THEN LINE TYPE 8
610   MOVE T(1),Mass1(1)
620   FOR I=2 TO N
630   DRAW T(I),Mass1(I)
640   NEXT I
650   PENUP
660   Plot=Plot+1
670   GOTO 60
700 Exit:   IF Plotter=2 THEN OUTPUT 7,5;"SP0/IN"
710   IF Plotter=2 THEN STOP
720   DUMP GRAPHICS
730   EXIT GRAPHICS
740   GCLEAR
750   END
760 Printer:    PRINTER IS 0
765  PRINT PAGE
770   PRINT LIN(2)
780   PRINT B$
785   PRINT USING 790;M0,Hrate,Sens
790   IMAGE "Initial mass is ",DDD.DD," mg.  Heating rate is ",DD," deg/min", ,
 "Sensitivity is ", DD," mg/mv"
800   PRINT LIN(2)
810   PRINT "Temperature (C)    Time(min)     Mass(mg)      % Mass Loss
   Data Pt #"
820   PRINT
830   FOR I=1 TO N
835   IF Mass(I)<0 THEN Mass(I)=0
836   IF Mass1(I)>100 THEN Mass1(I)=100
840   PRINT USING 860;T(I),Time(I),Mass(I),Mass1(I),I
850   NEXT I
860   IMAGE DDDD16X,DDD.DD8X,DD.D10X,DDD.DD12X,DDD
870   PRINT PAGE
880   RETURN
1000  DATA  .927763167,169526.515,-31563363.94,3990730633,-1.63565E12,1.38027E14
,-1.27241E16,6.17501E17,-1.56105E19,1.69535E20
1065 DEF FNScal(Z)
1075  COM A(0:9)
```

```
1085    Interpolating polynmial for converting millivolts to degrees
1095    for type S (platinum-10%rhodium / platinum) thermocouple.
1105  Scal=A(0)+Z*(A(1)+Z*(A(2)+Z*(A(3)+Z*(A(4)+Z*(A(5)+Z*(A(6)+Z*(A(7)+Z*(A(8)+
Z*A(9)))))))))
1115  RETURN Scal
1125  FNEND
1155  SUB Store(X(*),Y(*),Y0,N,Id$)
1165  SHORT A(N),B(N)
1175  MAT A=X
1185  MAT B=Y
1195  LINPUT "ENTER  FILE NAME",D$
1210  LINPUT "ENTER MASS STORAGE MEDIUM",E$
1215  CREATE D$&":"&E$,N/16+2
1225  ASSIGN #4 TO D$&":"&E$
1235  PRINT #4;Id$,Y0,N
1245  MAT PRINT #4;A,B
1255  ASSIGN #4 TO *
1265  SUBEXIT
1275  SUBEND
1300  SUB Continue
1305  OPTION BASE 1
1310  COM T(*),Mass(*),Mass1(*),Time(*),N,M0,A$,B$
1320  COM A(*),B(*),Anew(*),Bnew(*),Deriv(*)
1325  DIM Page$[80]
1330  CALL Plotter(B$,Time(*),Mass1(*),N,2)
1340  PRINT PAGE
1350  LINPUT "DO YOU WANT TO CONTINUE WITH DATA ANALYSIS?",Y$
1360  IF Y$[1,1]<>"Y" THEN SUBEXIT
1370  INPUT "ENTER BEGINNING AND ENDING POINT FOR DATA ANALYSIS",P1,P2
1380  Dim=P2-P1+1
1390  REDIM A(Dim),B(Dim),Deriv(Dim-1),Anew(Dim-1),Bnew(Dim-1)
1400  FOR K=1 TO Dim
1410  A(K)=T(P1+K-1)
1420  B(K)=Mass(P1+K-1)
1430  NEXT K
1440  FOR I=1 TO Dim-1   ! Calculate derivatives at midpoints.
1450  Anew(I)=(A(I+1)+A(I))/2
1460  NEXT I
1470  Eps=1E-6
1480  PRINT PAGE
1490  PRINT LIN(3)
1500  PRINT B$
1510  PRINT "Subset Output"
1520  PRINT LIN(2)
1530  CALL Spline(Dim,Dim-1,A(*),B(*),Anew(*),Bnew(*),Deriv(*),01,Eps)
1540  MAT Deriv=ABS(Deriv)
1550  Page$="Temperature(C)   Mass(mg)     -dM/dT        ln(dM/dT)"
1560  PRINT Page$
1570  PRINT LIN(2)
1580  FOR I=1 TO Dim-1
1590  PRINT USING 1670;I,Anew(I),Bnew(I),Deriv(I),LOG(Deriv(I))
1600  IF I MOD 50<>0 THEN GOTO 1660
1610  PRINT PAGE
1620  PRINT B$
1630  PRINT LIN(2)
1640  PRINT Page$
1650  PRINT LIN(2)
1660  NEXT I
1670  IMAGE DDDXXX,DDDDXXXXXX,MDD.DDDXXXXXX,MD.DDEXXXXXX,MZ.DDD
1680  CALL Plotter(B$,A(*),B(*),Dim,0)
1690  CALL Plotter(B$,Anew(*),Deriv(*),Dim-1,1)
1700  PRINT PAGE
1710  PRINT LIN(2)
1720  LINPUT "DO YOU WANT TO CALCULATE KINETIC PARAMETERS FROM THE DATA?",S$
1730  IF S$[1,1]="Y" THEN CALL Kinetics(B$,Anew(*),Bnew(*),Deriv(*),Dim,M0)
```

```
1740  GOTO 1350
1750  SUBEND
1800 SUB Plotter(A$,X(*),Y(*),N,Flag)
1801  INPUT "ENTER PLOTTER CODE:  1=CRT   2=9872A",Plotter
1802  IF Plotter=2 THEN PLOTTER IS 7,5,"9872A"
1803  IF Flag=2 THEN G$="Time(minutes)"
1805  IF Flag<2 THEN G$="Temperature (C)"
1806   IF Flag=0 THEN H$="Milligrams"
1807  IF Flag=1 THEN H$="Milligrams/deg"
1808  IF Flag=2 THEN H$="Percent Mass Loss"
1810 PRINTER IS 0
1811  PRINT PAGE
1812  PRINT
1813  PRINT A$
1814  IF Flag=1 THEN PRINT "Derivative Plot"
1815  PRINT LIN(2)
1816  IF Flag=0 THEN INPUT "ENTER MAXIMUM ORDINATE VALUE (mg)",C
1817  D=0
1818  IF Flag=2 THEN C=100
1819  IF Flag=1 THEN GOTO 1821
1820  LINPUT "DO YOU WANT COMPUTER CALCULATED ORDINATE TICKS?",Axis$
1821  IF Flag=1 THEN Axis$="Y"
1825 A=FNMax(X(*),N)
1830 B=FNMin(X(*),N)
1835  IF Axis$[1,1]<>"Y" THEN GOTO 1860
1840 C=FNMax(Y(*),N)
1850 D=FNMin(Y(*),N)
1860 E=(A-B)/10
1870 F=(C-D)/10
1871  IF Plotter=1 THEN PLOTTER IS "GRAPHICS"
1872  GRAPHICS
1880  IF Plotter=1 THEN LOCATE 20,90,20,90
1885  IF Plotter=2 THEN LOCATE 20,90,20,65
1890 SCALE B,A,D,C
1900  AXES 2*E,2*F,B,D
1910  MOVE X(1),Y(1)
1920  FOR I=1 TO N
1930  DRAW X(I),Y(I)
1940  NEXT I
1950  MOVE B,D-F
1960  LORG 6 !LABEL X AXIS
1970  FOR I=B TO A STEP 2*E
1980  MOVE I,D-.1*F
1990  LABEL USING "DDD";I
2000  NEXT I
2010  MOVE B,D-F
2020  DEG
2030  LORG 8 ! LABEL Y AXIS
2040  FOR I=D+2*F TO C STEP 2*F
2050  MOVE B-.1*E,I
2055  IF Flag=1 THEN LABEL USING "D.DDE";I
2060  IF Flag=0 THEN LABEL USING "DDD.DD";I
2065  IF Flag=2 THEN LABEL USING "DDD";I
2070  NEXT I
2080  LORG 6
2090  MOVE B+5*E,D-.8*F
2100  LABEL G$
2110  MOVE B+.4*E,D+5*F
2115  LORG 4
2120  LDIR 90
2130  LABEL H$
2131  LDIR 0
2132  IF Plotter=2 THEN OUTPUT 7,5;"IN"
2133  LINPUT "DO YOU WANT GRAPHICS OUTPUT ON THERMAL PRINTER",Print$
2134  IF Print$[1,1]="Y" THEN DUMP GRAPHICS
```

```
2135  CLEAR
2136  EXIT GRAPHICS
2139  LINPUT "DO YOU WANT THE PLOT REPEATED?",Rpt$
2144  IF Rpt$[1,1]="Y" THEN GOTO 1901
2149  SUBEXIT
2150  SUBEND
2160  DEF FNMax(X(*),N)
2170  Max=X(1)
2180  FOR I=2 TO N
2190  IF X(I)>Max THEN Max=X(I)
2200  NEXT I
2210  RETURN Max
2220  FNEND
2230  DEF FNMin(X(*),N)
2240  Min=X(1)
2250  FOR I=2 TO N
2260  IF X(I)<Min THEN Min=X(I)
2270  NEXT I
2280  RETURN Min
2290  FNEND
2300  SUB Insert(B$,X(*),Y(*),N)
2390  SUBEXIT
2400  SUBEND
2500  DEF FNScal(X)
2800 SUB Spline(N,Narg,X(*),Y(*),Domain(*),Func(*),Deriv(*),Int,Eps)
2880 Baddta=(Eps<=0)
2890 IF Baddta=0 THEN 2990
2920 PRINT LIN(2),"ERROR IN SUBPROGRAM Spline."
2930 PRINT "Eps=";Eps,LIN(2)
2940 PAUSE
2950 GOTO 2880
2990 OPTION BASE 1
3000 DIM S(N),G(N-1),Work(N-1)
3010 FOR I=2 TO N-1
3020     Xi=X(I)
3030     Ximl=X(I-1)
3040     Xipl=X(I+1)
3050     Yi=Y(I)
3060     Yiml=Y(I-1)
3070     Yipl=Y(I+1)
3080     X=Xi-Ximl
3090     H=Xipl-Ximl
3100     Work(I)=.5*X/H
3110     T=((Yipl-Yi)/(Xipl-Xi)-(Yi-Yiml)/X)/H
3120     S(I)=2*T
3130     G(I)=3*T
3140 NEXT I
3150 S(1)=S(N)=0
3170 W=8-4*SQR(3)
3180 U=0
3190 FOR I=2 TO N-1
3200     T=W*(-S(I)-Work(I)*S(I-1)-(.5-Work(I))*S(I+1)+G(I))
3210     H=ABS(T)
3220     IF H>U THEN U=H
3230     S(I)=S(I)+T
3240 NEXT I
3250 IF U>=Eps THEN 3180
3260 FOR I=1 TO N-1
3270     G(I)=(S(I+1)-S(I))/(X(I+1)-X(I))
3280 NEXT I
3290 IF Narg=0 THEN 3600
3330 FOR J=1 TO Narg
3340 Corrector:    I=1
3350     T=Domain(J)
3360     IF T>=X(1) THEN 3430
3370     PRINT LIN(2),"ERROR IN SUBPROGRAM Spline."
```

```
3380    PRINT "ARGUMENT OUT OF BOUNDS."
3390    PRINT "X(1)=";X(1),"X(N)=";X(N),"Domain(";J;")=";Domain(J),LIN(2)
3400    PAUSE
3430    I=I+1
3440    IF I>N THEN 3370
3450    IF T>X(I) THEN 3430
3460    I=I-1
3470    H=Domain(J)-X(I)
3480    T=Domain(J)-X(I+1)
3490    X=H*T
3500    S=S(I)+H*G(I)
3510    Z=1/6
3520    U=Z*(S(I)+S(I+1)+S)
3530    W=(Y(I+1)-Y(I))/(X(I+1)-X(I))
3540    Func(J)=W*H+Y(I)+X*U
3550    Deriv(J)=W+(H+T)*U+Z*X*G(I)
3560 NEXT J
3600 Int=0
3610 FOR I=1 TO N-1
3620    H=X(I+1)-X(I)
3630    Int=Int+.5*H*(Y(I)+Y(I+1))-1/24*H^3*(S(I)+S(I+1))
3640 NEXT I
3650 SUBEND
3800  SUB Kinetics(A$,X(*),Y(*),Z(*),N,Mz)
3802  REM X=TEMP, Y=MASS, Z=dM/dT
3804  OPTION BASE 1
3809  DIM Ff(N),Tinv(N),Xx(N),Yy(N),Dm(N)
3814  INPUT "ENTER RESIDUE MASS (mg)",Residue
3820  Mr=Mz-Residue ! Total mass reacted.
3824  INPUT "ENTER POINT NUMBERS FOR KINETICS PLOTS",P1,P2
3829  Datapoints=P2-P1+1
3831  REDIM Ff(Datapoints),Tinv(Datapoints),Xx(Datapoints),Yy(Datapoints),Dm(Dat
apoints)
3834  FOR I=1 TO Datapoints
3839  Xx(I)=X(P1+I-1)+273 ! Compute array and change to Kelvin.
3842  Yy(I)=Mz-Y(P1+I-1) ! Compute mass reacted array.
3844  Ff(I)=Yy(I)/Mr !Calculate fraction decomposed.
3845  Tinv(I)=1/Xx(I) !Calculate reciprocal temperature.
3846  NEXT I
3850  CALL Spline(Datapoints,Datapoints,Xx(*),Ff(*),Xx(*),Ff(*),Dm(*),Q2,1E-6)!F
it curve and calculate d(frac)/dT
3855  MAT Dm=ABS(Dm)
3860  CALL Plotz(Datapoints,Xx(*),Ff(*),Dm(*),A$)!Print and plot dx/dT vs x
3864  FOR I=1 TO Datapoints
3869  IF Dm(I)>.001 THEN Dm(I)=LOG(1000*Dm(I))
3874  NEXT I
3880  PRINT PAGE
3885  PRINT A$
3886  PRINT LIN(2)
3890  PRINT "Linear regression analysis of TGA data between Temperatures"
3900  PRINT USING 3910;Xx(1),Xx(Datapoints)
3910  IMAGE DDDD," and ",DDDD," degrees Kelvin."
3920  PRINT
3930  CALL Regress(Tinv(*),Dm(*),Datapoints,A,B,C1,C2,C3,C4,C5,C6,C7,C8,C9,C0,Va
r)
3940  PRINT USING 3950;ABS(B*1.9872),Var
3950  IMAGE "CALCULATED ACTIVATION ENERGY IS ",MD.DDE," Cal./mole "," +/- ",D.DD
E
3951  PRINT
4110  PRINT PAGE
4120  PRINT LIN(3)
4130  PRINT A$
4140  PRINT
4150  PRINT "KINETICS DATA PLOT"
4160  PRINT LIN(2)
4170  Xmax=FNMax(Tinv(*),Datapoints)
```

```
4180  Xmin=FNMin(Tinv(*),Datapoints)
4190  Ymax=FNMax(Dm(*),Datapoints)
4200  Ymin=FNMin(Dm(*),Datapoints)
4210  E=(Xmax-Xmin)/10
4220  F=(Ymax-Ymin)/10
4222  INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
4224  IF Code=2 THEN PLOTTER IS 7,5,"9872A"
4230  IF Code=1 THEN PLOTTER IS "GRAPHICS"
4240  GRAPHICS
4250  LOCATE 10,90,15,75
4260  SCALE Xmin,Xmax,Ymin-F,Ymax+F
4270  AXES 2*E,2*F,Xmin,Ymin-F
4280  FOR I=1 TO Datapoints
4290  MOVE Tinv(I),Dm(I)
4300  LABEL "+"
4310  NEXT I
4320  FOR J=1 TO Datapoints
4330  Dm(J)=B*Tinv(J)+A
4340  NEXT J
4350  MOVE Tinv(1),Dm(1)
4360  FOR I=1 TO Datapoints
4370  DRAW Tinv(I),Dm(I)
4380  NEXT I
4390  MOVE Xmin,Ymin-F
4400  LORG 6
4410  FOR I=Xmin TO Xmax STEP 2*E
4420  MOVE I,Ymin-1.1*F
4430  LABEL USING "D.DDD";I*1000
4440  NEXT I
4450  MOVE Xmin,Ymin-F
4460  LORG 8
4470  FOR I=Ymin+F TO Ymax+F STEP 2*F
4480  MOVE Xmin-.04*E,I
4490  LABEL USING "D.DDD";I
4500  NEXT I
4510  LORG 6
4520  MOVE Xmin+5*E,Ymin-2*F
4530  LABEL "1/T(K) x 1000"
4540  MOVE Xmin+.4*E,Ymin+5*F
4550  LDIR PI/2
4560  LABEL "ln (dM/dT) x 1000"
4570  PAUSE
4574  LINPUT "DO YOU WANT TO REPEAT THE PLOT?",Rpt$
4579  IF Rpt$[1,1]="Y" THEN GOTO 4222
4584  IF Code=1 THEN DUMP GRAPHICS
4594  EXIT GRAPHICS
4600  GCLEAR
4604  LINPUT "DO YOU WANT TO REPEAT USING DIFFERENT POINTS?",Again$
4608  IF Again$[1,1]="Y" THEN GOTO 3824
4610  SUBEXIT
4620  SUBEND
4700 SUB Regress(X(*),Y(*),N,A,B,Regss,Resss,Totalss,Regms,Resms,F,Dfreg,Dfres,D
ftot,Abort,Dev)
4710 ! *** MODEL: Y=A+B*X ***
4720 ON ERROR GOTO Bomb
4730 Abort=0
4740 Y1=X1=Z=X2=Y2=0
4750 FOR I=1 TO N
4760     X1=X1+X(I)                ! Sum of X's
4770     Y1=Y1+Y(I)                ! Sum of Y's
4780     X2=X2+X(I)*X(I)           ! Sum of X squares
4790     Y2=Y2+Y(I)*Y(I)           ! Sum of Y squares
4800     Z=Z+X(I)*Y(I)             ! Sum of XY's
4810 NEXT I
4820 X1=X1/N                       ! Mean X
4830 Y1=Y1/N                       ! Mean Y
```

```
4840 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
4850 A=Y1-B*X1
4860 Totalss=Y2-N*Y1*Y1              ! Total Sum of Squares
4870 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1)! Regression Sum of Squares
4880 Resss=Totalss-Regss             ! Residual Sum of Squares
4890 Regms=Regss                     ! Regression Mean Squares
4900 Resms=Resss/(N-2)               ! Residual Mean Squares
4904 Dev=SQR(Resms)                  ! Mean Square Deviation
4910 OFF ERROR
4920 DEFAULT ON
4930 F=Regms/Resms                   ! F Ratio
4940 DEFAULT OFF
4950 Dfreg=1                         ! Degrees of Freedom
4960 Dfres=N-2
4970 Dftot=Dfreg+Dfres
4980 SUBEXIT
4990 Bomb: Abort=1
5000 SUBEND
5330 SUB Exponential(X(*),Y(*),N,A,B,Regss,Resss,Totalss,Regms,Resms,F,Dfreg,Dfr
es,Dftot,Abort)
5340 ! *** MODEL: Y=A*EXP(B*X) ***
5350 ON ERROR GOTO Bomb
5360 Abort=0
5370 X1=X2=Z=Y1=Y2=0
5380 FOR I=1 TO N
5390    Logy=LOG(Y(I))
5400    X1=X1+X(I)                   ! Sum of X's
5410    X2=X2+X(I)*X(I)              ! Sum of X squares
5420    Y1=Y1+Logy                   ! Sum of Y's
5430    Y2=Y2+Logy*Logy              ! Sum of Y squares
5440    Z=Z+X(I)*Logy                ! Sum of XY's
5450 NEXT I
5460 X1=X1/N                         ! Mean X
5470 Y1=Y1/N                         ! Mean Y
5480 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
5490 A=EXP(Y1-B*X1)
5500 Totalss=Y2-N*Y1*Y1              ! Total Sum of Squares
5510 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1)! Regression Sum of Squares
5520 Resss=Totalss-Regss             ! Residual Sum of Squares
5530 Regms=Regss                     ! Regression Mean Squares
5540 Resms=Resss/(N-2)               ! Residual Mean Squares
5550 OFF ERROR
5560 DEFAULT ON
5570 F=Regms/Resms                   ! F Ratio
5580 DEFAULT OFF
5590 Dfreg=1                         ! Degrees of Freedom
5600 Dfres=N-2
5610 Dftot=Dfreg+Dfres
5620 SUBEXIT
5630 Bomb: Abort=1
5640 SUBEND
5650  SUB Plotz(N,T(*),X(*),Y(*),A$)
5660  OPTION BASE 1
5670  PRINT PAGE
5680  PRINT LIN(3)
5690  PRINT A$
5695  LINPUT "DO YOU WANT THE DATA PRINTED?",Print$
5696  IF Print$[1,1]="Y" THEN GOSUB Print
5700  PRINT "Kinetics plot of dx/dT vs. x.  x= fraction decomposed"
5710  PRINT LIN(3)
5720  C=FNMax(Y(*),N)
5730  D=FNMin(Y(*),N)
5740  E=.1
5750  F=(C-D)/10
5754  INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A ",Code
```

```
5760  IF Code=1 THEN PLOTTER IS "GRAPHICS"
5764  IF Code=2 THEN PLOTTER IS 7,5,"9872A"
5770  GRAPHICS
5780  LOCATE 25,90,15,75
5790  SCALE 0,1,D,C
5800  AXES .2,2*F,0,D
5810  FOR I=1 TO N
5820  MOVE X(I),Y(I)
5830  LABEL "+"
5840  NEXT I
5850  LORG 6
5860  FOR I=0 TO 1 STEP .2
5870  MOVE I,D-.1*F
5880  LABEL USING "Z.DDD";I
5890  NEXT I
5900  LORG 8
5910  FOR I=D+2*F TO C STEP 2*F
5920  MOVE -.01,I
5930  LABEL USING "D.DDE";I
5940  NEXT I
5950  LORG 6
5960  MOVE .5,D-.8*F
5970  LABEL "Fraction Decomposed"
5990  LDIR PI/2
6000  MOVE .025,D+5*F
6010  LABEL "Rate (mg/deg)"
6020  LDIR 0
6030  PAUSE
6040  IF Code=1 THEN DUMP GRAPHICS
6050  GCLEAR
6054  LINPUT "DO YOU WANT TO REPEAT THE PLOT?",Rpt$
6055  IF Rpt$[1,1]="Y" THEN GOTO 5700
6060  EXIT GRAPHICS
6070  SUBEXIT
6080 Print: PRINTER IS 0
6090  PRINT "Temperature(K)  Fraction decomposed     Rate (deg^-1)"
6100  PRINT
6110  FOR I=1 TO N
6120  PRINT USING 6150;T(I),X(I),Y(I)
6130  NEXT I
6150  IMAGE DDDDXXXXXXXXXXXXX,Z.DDDDXXXXXXXXXXXXXXXXXX,D.DDDE
6160  PRINT PAGE
6170  PRINT LIN(3)
6180  PRINT A$
6190  RETURN
6200  SUBEND
```

Appendix B

Program for Acquisition of Isothermal DSC Data

PROGRAM FOR ACQUISITION AND ANALYSIS OF ISOTHERMAL DSC DATA

```
10  OPTION BASE 1
20  DIM Y(1000),Time(1000),X3(1000),Y3(1000)
30  PRINTER IS 16
40  PRINT LIN(4)
50  PRINT "Data aquisition program for the Scanning Differential"
60  PRINT "Calorimeter.  Use scanning digital voltmeter line"
70  PRINT "9. Ordinate axis is calibrated for 10 millivolts"
80  PRINT "full scale."
90  PRINT "Data is taken at the approximate rate of one point"
100  PRINT "per 4 seconds. Edit line 310 to change rate"
110  PRINT
120  PRINT "Follow the CRT prompts.  Press CONT to enter data"
130  PRINT "into the computer or to have a plot on the CRT put"
140  PRINT "onto the thermal printer. Terminate the program by pressing"
145  PRINT "STOP."
146  PRINT
150  PRINT "EDIT THE PROGRAM AND PRESS CONT"
155  PAUSE
160  PRINT PAGE
170  PRINTER IS 0
180  DIM A$[60],B$[60],C$[80]
190  LINPUT " ENTER TEST IDENTIFIER, LINE 1",A$
200  LINPUT "ENTER TEST IDENTIFIER, LINE 2",B$
210  INPUT " ENTER TEMPERATURE OF THE RUN",Tinit
225  INPUT "ENTER MASS OF SAMPLE (mg)",Samplemass
226   INPUT "ENTER SENSITIVITY (mcal/sec)",Sensitivity
240  PRINT LIN(3)
250  PRINT A$
260  PRINT B$
270  PRINT USING 280;Tinit
275  PRINT USING 285;Samplemass,Sensitivity
280 IMAGE  "Temperature is  ",DDD," K "
285  IMAGE "Mass of sample is  ",DD.DDD," mg.  Sensitivity is ",DD," mcal/sec"
290   PRINT LIN(2)
300   REM  The following lines configure the scanning digital voltmeter and time
clock  and set key interupts.
310   OUTPUT 701;"R H2 0"!Configure DVM for interupt transfer.
320   ON ERROR GOSUB Escape!Enable run errors to be corrected.
330   ON KEY #7 GOSUB End!Operator termination of data aquisition.
335   ON KEY #8 GOSUB Exit
340   ON INT #7 GOSUB Read!Branching routine for data transfer.
350   OUTPUT 9;"A/U1=I2"!Configure clock.
360   CONTROL MASK 7;128!Look for interupt flag.
370   PRINT LIN(2)
375   PRINT "Time(sec)       Ordinate     Point#"
380   PRINT
385   I=1
390   DISP "Press CONT to begin data aquisition"
400   PAUSE
410   OUTPUT 9;"U1G"!Start the clock
420   DISP "PRESS K7 TO TERMINATE DATA GATHERING"
430   CARD ENABLE 7!Allow DVM interupts to take place.
440   IF I<1000 THEN GOTO 440
450   DISABLE
460   PRINTER IS 16
470   PRINT "ALLOCATED CORE STORAGE IS FULL"
480   PRINTER IS 0
```

```
490   GOSUB End
500 Exit:   OUTPUT 701;"*"
505   STOP
510 Read:     ! INPUT DATA FROM DSC
520   ENTER 701;Y(I)
525   Y(I)=Y(I)*1000+20 !Convert millivolts to a 0 to 10 scale.
530   OUTPUT 9;"U1V"
540   ENTER 9;Time(I)
550   Time(I)=Time(I)/1000 !Convert milliseconds to seconds.
560   PRINT USING 570;Time(I),Y(I),I
570   IMAGE DDDDXXXXXXXXXXXX,MDD.DDXXXXXXX,DDDD
580   I=I+1
650   OUTPUT 701;"0" !Trigger Digital Voltmeter
660   CARD ENABLE 7  !Re-Enable Interupts
670   RETURN
680 End:  !  Process Data
685  INPUT "ENTER POINT NUMBER OF STABLE ORDINATE",R
687  FOR K=1 TO R-1
690  Y(K)=Y(R)  !Eliminate initial transient
695  NEXT K
700   Npts=I-2  !Eliminate extraneous data points
710   REDIM Y(Npts),Time(Npts)  !Condense the arrays.
720   Minimum=FNMin(Y(*),Npts)  !Calculate lowest voltage output from DSC.
730   MAT Y=Y-(Minimum) !Set zero point as lowest output voltage
770   CALL Graph(A$,B$,Time(*),Y(*),Npts)  ! Plot the data.
780   LINPUT "DO YOU WANT THE DATA STORED?",C$
790   IF C$[1,1]="Y" THEN CALL Store(A$,B$,Time(*),Y(*),Npts)
800   LINPUT "DO YOU WANT TO EXPAND THE PLOT",D$
810   IF D$[1,1]="Y" THEN CALL Expand(A$,B$,Time(*),Y(*))
820   LINPUT "DO YOU WANT TO MAKE A LINEAR BASELINE CORRECTION?",E$
830   IF E$[1,1]="Y" THEN CALL Transform(A$,B$,Time(*),Y(*),Npts)
835   PRINTER IS 16
836   PRINT PAGE
837   PRINT "Peak integrator using an arbitrary baseline correction"
838   PRINT
839   PRINT "Data point numbers correspond to origional data list"
840   PRINT LIN(2)
841   PRINT "The baseline is calculated using a staight line from the first to
the last data point"
842   PRINT LIN(3)
843   PRINT "Press STOP if you wish to terminate the program.  Press CONT if
 you    wish to continue."
844   PAUSE
845   PRINT PAGE
846   INPUT "ENTER BEGINNING AND ENDING POINTS FOR NUMERICAL INTEGRATION",Begin,
End
850    Qpts=End-Begin+1
852    PRINT USING 854;Qpts
854    IMAGE "ENTER 1 AND ",DDD," FOR INTEGRATION LIMITS"
856    REDIM X3(Qpts),Y3(Qpts)
858    FOR L=1 TO Qpts
860    Y3(L)=Y(L+Begin-1)
862    X3(L)=Time(L+Begin-1)
864    NEXT L
866    Slope3=(Y3(Qpts)-Y3(1))/(X3(Qpts)-X3(1))
867    B=Y3(1)
868    FOR L=1 TO Qpts
870    Y3(L)=Y3(L)-Slope3*(X3(L)-X3(1))-B
872    NEXT L
874    C$=B$&": Expanded plot peak integration"
876    CALL Graph2(A$,C$,X3(*),Y3(*),Qpts,Area)
878    LINPUT "DO YOU WANT TO TERMINATE THE PROGRAM?",Stop$
880   IF Stop$[1,1]="Y" THEN GOSUB Exit
881   CALL Kinetics(X3(*),Y3(*),Qpts,Area)
884   GOTO 300
885 Escape:  ! Correct any run errors.
```

```
890   PRINTER IS 16
900   PRINT EPRM$&" GENERATED.  EDIT PROGRAM AND PRESS CONT."
910   PAUSE
920   PRINTER IS 0
930   RETURN
1000  SUB Store(A$,B$,X(*),Y(*),N)
1010  OPTION BASE 1  !Subroutine for storing data from X-Y plotter input.
1011  SHORT U(N),V(N)
1012  MAT U=X
1013  MAT V=Y
1020  LINPUT "ENTER MASS STORAGE MEDIUM",F$
1030  LINPUT "ENTER 6 CHARACTER FILE NAME",G$
1040  G$=G$&":"&F$
1050  CREATE G$,N/9
1060  ASSIGN #2 TO G$
1070  PRINT #2;A$,B$,N
1080  MAT PRINT #2;X,Y
1090  PRINT LIN(5)
1095  PRINT USING 1100;TRIM$(G$)
1100  IMAGE "DATA IS STORED IN FILE  ",K," "
1110  ASSIGN #2 TO *
1120  SUBEXIT
1130  SUBEND
1200  SUB Graph(A$,B$,X(*),Y(*),N)
1210  PRINT PAGE      !Subroutine for plotting data from an X-Y plotter
1220  PRINT LIN(3)  !using the internal thermal printer.
1230  OPTION BASE 1
1240  PRINT A$
1250  PRINT B$
1260  PRINT LIN(3)
1270  DIM D$[19]
1275  C$="TIME (sec)"
1278  D$="Relative Millivolts"
1280  F=FNMax(Y(*),N,1)
1290  B=X(N)-X(1)
1300  A=F
1310  LINPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MAXIMUM",J$
1320  IF J$[1,1]="Y" THEN INPUT "ENTER Ymax",H
1325  IF J$[1,1]="Y" THEN A=H
1330  LINPUT "ENTER PLOTTER CODE: CRT=A, 9872A=B",Plot$
1340  IF Plot$[1,1]="B" THEN PLOTTER IS 7,5,"9872A"
1350  IF Plot$[1,1]="A" THEN PLOTTER IS "GRAPHICS"
1360  GRAPHICS
1370  LOCATE 18,93,10,75
1380  SCALE X(1),X(N),0,A
1390  AXES B/4,A/10,X(1),0
1400  MOVE X(1),Y(1)
1410  FOR I=1 TO N
1420  DRAW X(I),Y(I)
1430  NEXT I
1440  PENUP
1480  LORG 6
1490  FOR I=X(1) TO X(N) STEP B/4
1500  MOVE I,-A/100
1510  LABEL USING 1530:I
1520  NEXT I
1530  IMAGE DDD
1540  LORG 8
1550  FOR I=A/10 TO A STEP A/10
1560  MOVE -B/100+X(1),I
1570  LABEL USING 1590;I
1580  NEXT I
1590  IMAGE DD.D
1600  LORG 6
1610  MOVE B/2+X(1),-A/15
```

```
1620  LABEL C$
1630  LDIR PI/2
1640  LORG 4
1650  MOVE -B/9+X(1),A/2
1660  LABEL D$
1670  LINPUT "DO YOU WANT GRAPHICS PRINTOUT VIA THE THERMAL PRINTER?",L$
1680  IF L$[1,1]="Y" THEN DUMP GRAPHICS
1690  EXIT GRAPHICS
1700  GCLEAR
1705  IF Plot$[1,1]="B" THEN OUTPUT 705;"SP0/IN"
1710  SUBEXIT
1720  SUBEND
1730  DEF FNMax(A(*),N,Start)
1740  Max=A(Start)
1750  FOR I=Start TO N
1760  IF A(I)>Max THEN Max=A(I)
1770  NEXT I
1780  RETURN Max
1790  FNEND
2000  SUB Expand(C$,D$,X(*),Y(*))
2010  OPTION BASE 1
2020  DIM Z(1000),T(1000),R(1000),W(1000)
2025  DIM I$[80],R$[80]
2030  INPUT "ENTER LOWEST AND HIGHEST DATA POINTS FOR PLOT EXPANSION (P1,P2)",P1
,P2
2040  N=ABS(P2-P1)+1
2050  REDIM Z(N),T(N)
2060  FOR I=1 TO N
2070  Z(I)=X(I+P1-1)
2080  T(I)=Y(I+P1-1)
2090  NEXT I
2100  I$=D$&":Expanded Plot"
2110  LINPUT "IS THIS A BASELINE CORRECTED PLOT?",M$
2120  IF M$[1,1]<>"Y" THEN GOTO 2175
2130  IF M$[1,1]="Y" THEN CALL Printz(C$,I$,Z(*),T(*),N)
2140  IF M$[1,1]="Y" THEN CALL Graph2(C$,I$,Z(*),T(*),N,Area)
2141  PRINTER IS 16
2143  PRINT "DO YOU WANT TO INTEGRATE THIS EXPANDED PLOT USING ANOTHER BASELINE
CORRECTION?"
2144  LINPUT N$
2145  PRINT PAGE
2146  IF N$[1,1]<>"Y" THEN GOTO 2170
2147  INPUT "ENTER THE DATA POINT NUMBERS (new list) FOR ORDINATE POINTS ",P3,P4
2148  Mx=P4-P3+1
2149  REDIM R(Mx),W(Mx)
2150  PRINT USING 2152;Mx
2152  IMAGE "USE 1 AND ",DDD," FOR INTEGRATION LIMITS"
2153  FOR K=1 TO Mx
2154  R(K)=Z(K+P3-1)
2155  W(K)=T(K+P3-1)
2156  NEXT K
2157  R$="Expanded Plot:  Arbitrary baseline correction"
2158  Slope2=(W(Mx)-W(1))/(R(Mx)-R(1))
2159  Bb=W(1)
2162  FOR K=1 TO Mx
2163  W(K)=W(K)-Slope2*(R(K)-R(1))-Bb
2164  NEXT K
2165  CALL Graph2(C$,R$,R(*),W(*),Mx)
2170  IF M$[1,1]="Y" THEN SUBEXIT
2175  CALL Grapn(C$,I$,Z(*),T(*),N)
2180  SUBEXIT
2185  SUBEND
2190  SUB Transform(F$,G$,X(*),Y(*),N)
2200  OPTION BASE 1   ! Linear baseline correction for 2 variable plots.
2210  DIM Ynew(N)
2215  DIM H$[80]
```

```
2220  S=(Y(6)+Y(7)+Y(8)+Y(9)+Y(10))/5  ! Average the first and last 5 points and
take initial dip into consideration
2230  V=(Y(N)+Y(N-1)+Y(N-2)+Y(N-3)+Y(N-4))/5  ! for slope calculation.
2240  Slope=(V-S)/(X(N)-X(1))
2250  FOR I=1 TO N
2260  Ynew(I)=Y(I)-Slope*(X(I)-X(1))-S
2270  NEXT I
2280  H$=G$&"Linear Baseline Correction"
2290  CALL Graph2(F$,H$,X(*),Ynew(*),N,Area)
2330  LINPUT "DO YOU WANT THE PLOT EXPANDED?",N$
2335  IF N$[1,1]="Y" THEN CALL Expand(F$,H$,X(*),Ynew(*))
2340  SUBEXIT
2350  SUBEND
2400 DEF FNMaxabs(A(*),N)
2410  Maxabs=ABS(A(1))
2420  FOR I=2 TO N
2430  IF ABS(A(I))>Maxabs THEN Maxabs=ABS(A(I))
2440  NEXT I
2441  RETURN Maxabs
2442  FNEND
2450 DEF FNMin(B(*),N)
2460  Min=B(1)
2470  FOR I=2 TO N
2480  IF B(I)<Min THEN Min=B(I)
2490  NEXT I
2500  RETURN Min
2510  FNEND
2600  SUB Graph2(A$,B$,X(*),Y(*),N,Integral)
2605  PRINTER IS 0
2610  PRINT PAGE      !Subroutine for plotting data from an X-Y plotter
2620  PRINT LIN(3)  !using the internal thermal printer.
2630  OPTION BASE 1
2640  PRINT A$
2650  PRINT B$
2660  PRINT LIN(3)
2670  DIM D$[19],Ux(1000),Vy(1000)
2671  REDIM Ux(N),Vy(N)
2675  C$="TIME (sec)"
2678  D$="Relative Millivolts"
2680  F=FNMaxabs(Y(*),N)
2690  B=X(N)-X(1)
2700  A=F
2710  LINPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MAXIMUM",J$
2720  IF J$[1,1]="Y" THEN INPUT "ENTER Ymax",H
2740  IF J$[1,1]="Y" THEN A=H
2745  LINPUT "ENTER PLOTTER CODE: CRT=A, 9872A=B",Plot$
2750  IF Plot$[1,1]="A" THEN PLOTTER IS "GRAPHICS"
2755  IF Plot$[1,1]="B" THEN PLOTTER IS 7,5,"9872A"
2760  GRAPHICS
2770  LOCATE 17,92,10,75
2780  SCALE X(1),X(N),-A,A
2790  AXES B/4,A/10,X(1),0
2800  MOVE X(1),Y(1)
2810  FOR I=1 TO N
2820  DRAW X(I),Y(I)
2830  NEXT I
2840  PENUP
2880  LORG 6
2890  FOR I=X(1) TO X(N) STEP B/4
2900  MOVE I,-A/100
2910  LABEL USING 2930;I
2920  NEXT I
2930  IMAGE DDD
2940  LORG 8
2950  FOR I=-A TO A STEP A/10
```

```
2960  MOVE -B/100+X(1),I
2970  LABEL USING 2990;I
2980  NEXT I
2990  IMAGE MDD.D
3000  LORG 6
3010  MOVE B/2+X(1),-A/15
3020  LABEL C$
3030  LDIR PI/2
3040  LORG 4
3050  MOVE -B/9+X(1),A/2
3060  LABEL D$
3062  LINPUT "DO YOU WANT TO INTEGRATE PART OF THE CURVE",O$
3065  IF O$[1,1]<>"Y" THEN GOTO 3085
3066  INPUT "ENTER BEGINNING AND ENDING DATA POINT NUMBERS(FROM NEW SET IF EXPAN
DED)",Start,Finish
3067  REDIM Ux(Finish-Start+1),Vy(Finish-Start+1)
3068  J=1
3069  FOR I=Start TO Finish
3070  Ux(J)=X(I)
3071  Vy(J)=Y(I)
3072  MOVE X(I),Y(I)
3073  DRAW X(I),0
3074  PENUP
3075  J=J+1
3076  NEXT I
3077  Epsilon=1E-6
3078  CALL Intun(J-1,Epsilon,Ux(*),Vy(*),Integral)
3079  PRINT USING 3080;Ux(1),Ux(J-1),Integral
3080  IMAGE "THE AREA REPRESENTED BY THE SHADED REGION BETWEEN DOMAIN VALUES  ",
DDDD.DD,"   AND ",DDDD.DD," IS  ",MD.DDDE
3081  PRINT LIN(2)
3085  LINPUT "DO YOU WANT GRAPHICS PRINTOUT VIA THE THERMAL PRINTER?",L$
3090  IF L$[1,1]="Y" THEN DUMP GRAPHICS
3095  EXIT GRAPHICS
3100  GCLEAR
3105  IF Plot$[1,1]="B" THEN OUTPUT 7,5;"SP0/IN"
3110  SUBEXIT
3120  SUBEND
3130  SUB Printz(A$,B$,X(*),Y(*),N)
3140  OPTION BASE 1
3145  LINPUT "DO YOU WANT THIS PRINTED ON THE TYPEWRITER?",Printer$
3146  IF Printer$[1,1]="Y" THEN PRINTER IS 7,4
3147  GOTO 3160
3150  PRINT PAGE
3160  PRINT "DATA POINT RENUMBERING FOR BASELINE CORRECTED , EXPANDED PLOT"
3170  PRINT A$
3180  PRINT B$
3190  PRINT
3200  PRINT "DOMAIN VALUE     RANGE VALUE     NEW DATA POINT NUMBER"
3210  PRINT
3220  FOR I=1 TO N
3230  PRINT USING 3250;X(I),Y(I),I
3240  NEXT I
3250  IMAGE DDDD.DDXXXXXXXXXXX,DD.DDXXXXXXXXXXX,DDD
3260  PRINT LIN(6)
3270  SUBEXIT
3290  SUBEND
3400 SUB Intun(N,Eps,X(*),Y(*),Int) ! Cubic Spline Integrator
3480 Baddta=(N<=3) OR (X(1)>=X(N)) OR (Eps<=0)
3490 IF Baddta=0 THEN 3600
3520 PRINT LIN(2),"ERROR IN SUBPROGRAM Intun."
3530 PRINT USING 3540;N,Eps,X(1),X(N)
3540 IMAGE "N=",DDD,5X,"Eps=",MZ.6DE,/, "X(1)=",MZ.6DE,5X,"X(N)=",MZ.6DE,/
3550 PAUSE
3560 GOTO 3480
3600 OPTION BASE 1
```

```
3610 DIM B(2:N-1),S(N),G(2:N-1)
3620 FOR I=2 TO N-1
3630    H=X(I+1)-X(I-1)
3640    X=X(I)-X(I-1)
3650    B(I)=.5*X/H
3660    T=((Y(I+1)-Y(I))/(X(I+1)-X(I))-(Y(I)-Y(I-1))/X)/H
3670    S(I)=2*T
3680    G(I)=3*T
3690 NEXT I
3700 S(1)=S(N)=0
3720 W=8-4*SQR(3)
3740 U=0
3760 FOR I=2 TO N-1
3770    T=W*(-S(I)-B(I)*S(I-1)-(.5-B(I))*S(I+1)+G(I))
3780    H=ABS(T)
3800    IF H>U THEN U=H
3820    S(I)=S(I)+T
3830 NEXT I
3850 IF U>=Eps THEN 3740
3860 Int=0
3920 FOR I=1 TO N-1
3930    H=X(I+1)-X(I)
3940    Int=Int+(.5*H*(Y(I)+Y(I+1))-1/24*H^3*(S(I)+S(I+1)))
3950 NEXT I
3960 SUBEND
4000  SUB Kinetics(X2(*),Y2(*),N,D)
4010  OPTION BASE 1
4020  PRINTER IS 0
4040  DIM X4(N),Y4(N),A(4:N),Frac(4:N),Da(5:N),Deriv(5:N),Logd(N)
4090  Epsilon=1E-6    ! Establish tollerance for convergence
4110  FOR I=1 TO 3
4120  X4(I)=X2(I)
4130  Y4(I)=Y2(I)   ! Begin generating partial area arrays.
4140  NEXT I
4150  FOR J=4 TO N
4160  REDIM X4(J),Y4(J)  !Incrementally generate partial area arrays.
4170  X4(J)=X2(J)
4180  Y4(J)=Y2(J)
4190  CALL Intun(J,Epsilon,X4(*),Y4(*),A(J))
4200  Frac(J)=A(J)/D  !Calculate fractional areas.
4210  DISP "Generating Areas",J,A(J),Frac(J)
4215  NEXT J
4220  FOR K=5 TO N
4230  Da(K)=A(K)-A(K-1)
4240  Deriv(K)=Da(K)/(X2(K)-X2(K-1))
4250  NEXT K
4270  PRINT "TIME(s)  AREA   FRACT A   AREA INCREMENT   RATE OF INCREAS
E     Pt#"
4280  PRINT LIN(2)
4290  FOR I=5 TO N
4300  PRINT USING 4320;X2(I),A(I),Frac(I),Da(I),Deriv(I),I
4310  NEXT I
4320  IMAGE DDDDXXXXX,DDDDXXXXX,Z.DDDXXXXXX,DDZ.DDDXXXXXXXXXX,DDZ.DDDXXXXXXXXXX
,DDD
4330  CALL Plot(Frac(*),Deriv(*),N)
4340  MAT Y2=Y2+(1E-6)      !Insure nonzero arguments
4350  MAT Logd=LOG(Y2)
4365  CALL Printer(X2(*),Y2(*),Frac(*),Logd(*),N)
4370  CALL Plot2(X2(*),Frac(*),N)
4375  PRINT PAGE
4380  CALL Plot3(X2(*),Logd(*),N)
4390  PRINT PAGE
4400  CALL Plot4(Frac(*),Logd(*),N)
4490  SUBEXIT
4500  SUBEND
5000 SUB Linear(X(*),Y(*),N,A,B,Regss,Resss,Totalss,Regms,Resms,F,Dfreg,Dfres,Df
```

```
tot,Abort,Variance)
5010 ! *** MODEL: Y=A+B*X ***
5020 ON ERROR GOTO Bomb
5030 Abort=0
5040 Y1=X1=Z=X2=Y2=0
5050 FOR I=1 TO N
5060     X1=X1+X(I)                  ! Sum of X's
5070     Y1=Y1+Y(I)                  ! Sum of Y's
5080     X2=X2+X(I)*X(I)             ! Sum of X squares
5090     Y2=Y2+Y(I)*Y(I)             ! Sum of Y squares
5100     Z=Z+X(I)*Y(I)               ! Sum of XY's
5110 NEXT I
5120 X1=X1/N                         ! Mean X
5130 Y1=Y1/N                         ! Mean Y
5140 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
5150 A=Y1-B*X1
5160 Totalss=Y2-N*Y1*Y1              ! Total Sum of Squares
5170 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1)! Regression Sum of Squares
5180 Resss=Totalss-Regss             ! Residual Sum of Squares
5190 Regms=Regss                     ! Regression Mean Squares
5200 Resms=Resss/(N-2)               ! Residual Mean Squares
5205 Variance=SQR(Resms/(X2-N*X1*X1))
5210 OFF ERROR
5220 DEFAULT ON
5230 F=Regms/Resms                   ! F Ratio
5240 DEFAULT OFF
5250 Dfreg=1                         ! Degrees of Freedom
5260 Dfres=N-2
5270 Dftot=Dfreg+Dfres
5280 SUBEXIT
5290 Bomb: Abort=1
5300 SUBEND
5310 SUB Plot1(X(*),Y(*),N)
5320 ! Plot fraction reacted vs rate of reaction.
5330 Xmax=FNMax(X(*),N)
5340 Xmin=FNMin(X(*),N)
5350 Ymax=FNMax(X(*),N)
5360 Ymin=FNMin(X(*),N)
5370 LINPUT "ENTER PLOTTER CODE:A=CRT,B=9872A",Plotter$
5380 IF Plotter$[1,1]="A" THEN PLOTTER IS "GRAPHICS"
5390 IF Plotter$[1,1]="B" THEN PLOTTER IS 7,5,"9872A"
5400 GRAPHICS
5410 LOCATE 5,90,10,75
5420 SCALE Xmin,Xmax,Ymin,Ymax
5430 AXES (Xmax-Xmin)/4,(Ymax-Ymin)/4,Xmin,Ymin
5440 FOR I=1 TO N
5450 PLOT X(I),Y(I)
5460 NEXT I
5470 LORG 6
5480 FOR J=Xmin TO Xmax STEP (Xmax-Xmin)/4
5490 MOVE J,Ymin-Ymin/20
5500 LABEL USING "D.DDE";J
5510 NEXT J
5520 LORG 8
5530 FOR K=Ymin+(Ymax-Ymin)/4 TO Ymax STEP (Ymax-Ymin)/4
5540 MOVE Xmin-Xmin/20,K
5550 LABEL USING "D.DDE";K
5560 NEXT K
5570 MOVE Xmin,Ymin-(Ymax-Ymin)/8
5580 LORG 3
5590 LABEL "Plot of fraction reacted vs rate"
5595 PAUSE
5600 IF Plotter$[1,1]="A" THEN DUMP GRAPHICS
5605 IF Plotter$[1,1]="B" THEN OUTPUT 7,5;"SP0/IN"
5610 EXIT GRAPHICS
5615  GCLEAR
```

```
5616  SUBEXIT
5620 SUBEND
5630 SUB Plot2(X(*),Y(*),N)
5640 ! Plot (1-fraction reacted) vs time
5650 LINPUT "ENTER PLOTTEF CODE:A=CRT,B=9872A",Plotter$
5660 IF Plotter$[1,1]="A" THEN PLOTTER IS "GRAPHICS"
5670 IF Plotter$[1,1]="B" THEN PLOTTER IS 7,5,"9872A"
5680 IF Plotter$[1,1]="A" THEN PRINT PAGE
5690 GPAPHICS
5700 LOCATE 10,90,10,75
5710 SCALE X(5),X(N),0,1
5720  AXES (X(N)-X(5))/4,.25,X(5),0
5730  FOR I=5 TO N
5740  PLOT X(I),1-Y(I)
5750 NEXT I
5760 LORG 6
5770 FOP J=X(5) TO X(N) STEP (X(N)-X(5))/4
5780 MOVE J,-.02
5790 LABEL USING "DDDD";J
5800 NEXT J
5810 MOVE (X(N)-X(5))/2+X(5),-.07
5820 LABEL "Time (seconds)"
5830 LORG 8
5840 FOR K=.25 TO 1 STEP .25
5850 MOVE (X(N)-X(5))/20+X(5),K
5860 LABEL USING "Z.DD";K
5870 NEXT K
5880 LORG 3
5890 LDIR PI/2
5900 MOVE (X(N)-X(5))/20+X(5),.05
5910 LABEL "Fraction Unreacted"
5915 PAUSE
5920 IF Plotter$[1,1]="A" THEN DUMP GRAPHICS
5925 IF Plotter$[1,1]="B" THEN OUTPUT 7,5;"SP0/IN"
5930 EXIT GRAPHICS
5931  GCLEAR
5935 SUBEXIT
5940 SUBEND
5950 SUB Plot3(X(*),Y(*),N)
5960 ! Plot of log displacement vs time
5970 DIM A(N),B(N)  !Partial Arrays for Kinetics Calculations
5980 LINPUT "ENTEP PLOTTER CODE: A=CRT, B=9872A",Plotter$
5990 IF Plotter$[1,1]="A" THEN PLOTTER IS "GRAPHICS"
6000 IF Plotter$[1,1]="B" THEN PLOTTEP IS 7,5,"9872A"
6010 GRAPHICS
6020 LOCATE 10,90,10,75
6030 SCALE X(5),X(N),0,5
6035 LDIR 0
6040 AXES (X(N)-X(5))/4,1,X(5),0
6050 FOP I=5 TO N
6060  DRAW X(I),Y(I)
6070  NEXT I
6080 LOPG 6  ! Label the axes
6090  FOR I=X(5) TO X(N) STEF (X(N)-X(5))/4
6100  MOVE I,-.05
6110  LABEL USING "DDD";I
6120    NEXT I
6130  MOVE (X(N)-X(5))/2+X(5),-.3
6140  LABEL "Time (sec)"
6145  LORG 8
6150  FOR J=1 TO 5
6160  MOVE X(5)-.01*(X(N)-X(5)),J
6170  LABEL USING "D.D";J
6180  NEXT J
6190  LDIP PI/2
6200  LORG 6
```

```
6210  MOVE X(5)+.05*(X(N)-X(5)),2.5
6220  LABEL "Ln(displacement)"
6230  LDIR 0
6240  PAUSE
6250  IF Plotter$[1,1]="A" THEN DUMP GRAPHICS
6255  IF Plotter$[1,1]="B" THEN OUTPUT 7,5;"SP0/IN"
6260  EXIT GRAPHICS
6265  GCLEAR
6270  PRINTER IS 0
6275  INPUT "ENTER TWO POINT NUMBERS FOR THE SLOPE CALCULATION",S,T
6280  Nptsd=T-S+1
6285  REDIM A(1:Nptsd),B(1:Nptsd)
6290  PRINT LIN(3)
6295  FOR I=1 TO Nptsd
6300   A(I)=X(S+I-1)
6305   B(I)=Y(S+I-1)
6310  NEXT I
6320  CALL Linear(A(*),B(*),Nptsd,Int,Slp,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,Var)
6330  PRINT USING 6340;A(1),A(Nptsd),Slp,Var
6340 IMAGE "Slope of plot between times ",DDDD," and ",DDDD," seconds is "/D.DDE
," +/- ",D.DDE," sec-1"
6350   PRINT LIN(3)
6360   LINPUT "DO YOU WANT TO REPEAT THE CALCULATION USING OTHER POINTS?",Rpt$
6370   IF (Rpt$[1,1]="Y") OR (Rpt$[1,1]="y") THEN GOTO 6275
6375 SUBEXIT
6380 SUBEND
6600  SUB Plot(X(*),Y(*),N)
6610  REM  Plot dA/dt vs A and choose linear portion for kinetics
6620  PRINT PAGE
6625  OPTION BASE 1
6630  PRINT LIN(3)
6640  PRINT "Kinetics plot of dx/dt vs x.  x = fraction decomposed"
6650  DIM X1(N),Y1(N)
6660  C=FNMax(Y(*),N,5)
6690  F=C/10
6700  PLOTTER IS "GRAPHICS"
6710  GRAPHICS
6720  LOCATE 10,90,10,75
6730  SCALE 0,1,0,C
6740  AXES .25,2.5*F,0,0
6750  FOR I=5 TO N
6760  MOVE X(I),Y(I)
6770  LABEL "+"
6780  NEXT I
6790  LORG 6
6800  FOR I=0 TO 1 STEP .25
6810  MOVE I,-.1*F
6820  LABEL USING "Z.DD";I
6830  NEXT I
6840  LORG 8
6850  FOR I=2.5*F TO C STEP 2.5*F
6860  MOVE -.01,I
6870  LABEL USING "DZ.DD";I
6880  NEXT I
6890  LORG 6
6900  MOVE .5,-.8*F
6910  LABEL "Fraction Decomposed"
6920  LDIR PI/2
6930  MOVE .025,D+5*F
6940  LABEL "Relative Rate"
6950  LDIR 0
6960  PAUSE
6970  DUMP GRAPHICS
6980  GCLEAR
6990  EXIT GRAPHICS
7000  PRINT PAGE
```

```
7010  PRINT LIN(2)
7020  PRINT "Linear Regression Analysis of the Data"
7030  PRINT LIN(2)
7040  INPUT "ENTER BEGINNING AND ENDING POINT FOR CURVE FITTING",Begin,End
7050  Pts=End-Begin+1
7060  REDIM X1(1:Pts),Y1(1:Pts)
7070  FOR I=1 TO Pts
7080  X1(I)=X(Begin+I-1)
7090  Y1(I)=Y(Begin+I-1)
7100  NEXT I
7110  PRINT USING 7120;X1(1),X1(Pts)
7120  IMAGE "Plot is between times ",DDDD.D," seconds and ",DDDD.D," seconds."
7130  PRINT LIN(2)
7140  CALL Linear(X1(*),Y1(*),Pts,A,B,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,V)
7150  PRINT USING 7160;ABS(B),V
7160  IMAGE "Rate Constant is ",D.DDE, "sec-1.    Mean Variance is ",D.DDE
7170  PRINT LIN(3)
7180  Xmax=FNMax(X1(*),Pts,1)
7190  Ymax=FNMax(Y1(*),Pts,1)
7200  Xmin=FNMin(X1(*),Pts)
7210  Ymin=FNMin(Y1(*),Pts)
7220  E=(Xmax-Xmin)/10
7230  F=(Ymax-Ymin)/10
7240  PLOTTER IS "GRAPHICS"
7250  GRAPHICS
7260  LOCATE 20,100,20,90
7270  SCALE Xmin,Xmax,Ymin,Ymax
7280  AXES 2*E,2*F,Xmin,Ymin
7290  FOR I=1 TO Pts
7300  MOVE X1(I),Y1(I)
7310  LABEL "+"
7320  NEXT I
7330  FOR J=1 TO Pts
7340  Y1(J)=X1(J)*B+A
7350  NEXT J
7360  MOVE X1(1),Y1(1)
7370  FOR I=1 TO Pts
7380  DRAW X1(I),Y1(I)
7390  NEXT I
7400  LORG 6
7410  FOR I=Xmin TO Xmax STEP 2*E
7420  MOVE I,Ymin-.1*F
7430  LABEL USING "Z.DDD";I
7440  NEXT I
7450  LORG 8
7460  FOR I=Ymin+2*F TO Ymax STEP 2*F
7470  MOVE Xmin-.04*E,I
7480  LABEL USING "DZ.DD";I
7490  NEXT I
7500  LORG 6
7510  MOVE Xmin+5*E,Ymin-F
7520  LABEL "Fraction Decomposed"
7530  LDIR PI/2
7540  MOVE Xmin+.4*E,Ymin+5*F
7550  LABEL "Relative Rate"
7560  PAUSE
7570  DUMP GRAPHICS
7580  GCLEAR
7590  EXIT GRAPHICS
7600  LINPUT "DO YOU WANT TO REPEAT THE CALCULATION?",Repeat$
7610  IF Repeat$[1,1]="Y" THEN GOTO 7000
7620  SUBEXIT
7630  SUBEND
7700  DEF FNMon(A(*),N)
7710  Min=A(1)
7720  FOR I=1 TO N
```

```
7730  IF A(I)<Min THEN Min=A(I)
7740  NEXT I
7750  RETURN Min
7760  FNEND
7770  SUB Printer(Time(*),Disp(*),Frac(*),Logd(*),N)
7780  ! Print out values used in kinetics calculations
7790  DISP "CHOOSE PRINTER AND PRESS CONT"
7800  PAUSE
7810  PRINT "Pt#      Time(sec)       Y      Log(Y)       a       (1-a)      L
n 100*(1-a)"
7820  PRINT
7830  FOR I=5 TO N
7835  IF Frac(I)=1 THEN GOTO 7870
7840 PRINT USING 7860;I,Time(I),Disp(I),Logd(I),Frac(I),1-Frac(I),LOG(100*(1-Fra
c(I)))
7850  NEXT I
7860  IMAGE  DDDXXXXX,DDDDXXXXXX,DDD.DXXXXX,MZ.DDDXXXXX,Z.DDDXXX,Z.DDDXXXXX,MZ.D
DD
7870  PRINT PAGE
7880  SUBEXIT
7890  SUBEND
7900  SUB Plot4(X(*),Y(*),Z)
7901  DIM U(Z),V(Z)! order plot of log(displacement) vs log(100*(1-a))
7905  LINPUT "ENTER PLOTTER CODE: CRT=A, 9872A=B",Plotter$
7910  IF Plotter$[1,1]="A" THEN PLOTTER IS "GRAPHICS"
7915  IF Plotter$[1,1]="B" THEN PLOTTER IS 7,5,"9872A"
7920  MAT X=(1)-X
7925  MAT X=(100)*X  ! Eliminate negative logarithms
7930  FOR I=5 TO Z
7933  IF X(I)=0 THEN GOTO 7937
7935  X(I)=LOG(X(I))
7937  NEXT I
7940  A=5
7950  C=5
7970  LOCATE 15,90,10,80
7980  SCALE 0,A,0,C
7985  SHOW 0,A,0,C
7990  AXES 1,1,0,0
8000  FOR I=5 TO Z
8002  IF Y(I)<0 THEN Y(I)=0  ! Ignore negative logarithms.
8003  IF X(I)<0 THEN X(I)=0
8010  PLOT X(I),Y(I)
8020  NEXT I
8025  LORG 6
8030  FOR I=0 TO A
8040  MOVE I,-.02*C
8050  LABEL USING "Z.D";I
8060  NEXT I
8070  MOVE A/2,-.08*C
8080  LABEL "Ln(100*(1-a))"
8085  LORG 8
8090  FOR I=1 TO 5
8100  MOVE -.02*A,I
8110  LABEL USING "D.DD";I
8120  NEXT I
8130  LDIR PI/2
8140  MOVE .05*A,.5*C
8150  LORG 6
8160  LABEL "Ln(displacement)"
8170  PAUSE
8180  IF Plotter$[1,1]="A" THEN DUMP GRAPHICS
8190  IF Plotter$[1,1]="B" THEN OUTPUT 7,5;"SP0/IN"
8200  LDIR 0
8210  EXIT GRAPHICS
8220  GCLEAR
8230  INPUT "ENTER TWO POINTS FOR SLOPE CALCULATION",B,D
```

```
8240  Qpts=D-B+1
8250  REDIM U(1:Qpts),V(1:Qpts)
8260  FOR I=1 TO Qpts
8270  U(I)=X(B+I-1)
8280  V(I)=Y(B+I-1)
8290  NEXT I
8300  CALL Linear(U(*),V(*),Qpts,Int,Slope,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,Var)
8310  PRINT LIN(3)
8320  PRINT USING 8330;U(1),U(Qpts),Slope,Var
8330  IMAGE "Slope of order curve between values ",D.DD," and ",D.DD," is ",D.DD,
" + - ",Z.DDD
8340  LINPUT "DO YOU WANT TO REPEAT THE CALCULATION?",Again$
8350  IF Again$[1,1]="Y" THEN GOTO 8230
8360  SUBEXIT
8370  SUBEND
```

APPENDIX C

Program for Acquisition and Analysis of Thermogravimetric Data

PROGRAM FOR AQUISITION AND ANALYSIS OF CONSTANT HEATING RATE DIFFERENTIAL SCANNING CALORIMETER DATA.

```
10  OPTION BASE 1
20  DIM Y(1000),Temp(1000),X3(1000),Y3(1000)
30  PRINTER IS 16
40  PRINT LIN(4)
50  PRINT "Data aquisition program for the Scanning Differential"
60  PRINT "Calorimeter.  Use scanning digital voltmeter line"
70  PRINT "9. Ordinate axis is calibrated for 10 millivolts"
80  PRINT "full scale.  Temperature is calculated as TIME x "
90  PRINT "HEATING RATE.  Data is taken at the approximate rate"
100  PRINT "of one point per 4 seconds. Edit line 310 to change rate"
110  PRINT
120  PRINT "Follow the CRT prompts.  Press CONT to enter data"
130  PRINT "into the computer or to have a plot on the CRT put"
140  PRINT "onto the thermal printer. Terminate the program by pressing"
145  PRINT "STOP.  Edit k5 if you want additional graphics features."
146   PRINT
150  PRINT "EDIT THE PROGRAM AND PRESS CONT"
155  PAUSE
160  PRINT PAGE
170  PRINTER IS 0
180  DIM A$[60],B$[60],C$[80]
190  LINPUT " ENTER TEST IDENTIFIER, LINE 1",A$
200  LINPUT "ENTER TEST IDENTIFIER, LINE 2",B$
210  INPUT " ENTER INITIAL TEMPERATURE OF THE RUN  K ",Tinit
220  INPUT "ENTER THE HEATING RATE IN DEGREES C per MINUTE",Rate
225  INPUT "ENTER MASS OF SAMPLE (mg)",Samplemass
226   INPUT "ENTER SENSITIVITY (mcal/sec)",Sensitivity
230  Rate=Rate/60  !Convert rate to degrees per second.
240  PRINT LIN(3)
250  PRINT A$
260  PRINT B$
270  PRINT USING 280;Tinit,Rate*60
275  PRINT USING 285;Samplemass,Sensitivity
280 IMAGE  "Initial Temperature is  ",DDD," K   Heating Rate is ",DD," deg/min"
285  IMAGE "Mass of sample is  ",DD.DDD," mg.  Sensitivity is ",DD," mcal/sec"
290   PRINT LIN(2)
300   REM  The following lines configure the scanning digital voltmeter and time
clock and set key interupts.
310   OUTPUT 701;"R H0 0"!Configure DVM for interupt transfer.
320   ON ERROR GOSUB Escape!Enable run errors to be corrected.
330   ON KEY #7 GOSUB End!Operator termination of data aquisition.
335   ON KEY #8 GOSUB Exit
340   ON INT #7 GOSUB Read!Branching routine for data transfer.
350   OUTPUT 9;"A/U1=I2"!Configure clock.
360   CONTROL MASK 7;128!Look for interupt flag.
370   PRINT LIN(2)
375   PRINT "TEMPERATURE (K)    ORDINATE     POINT#"
380   PRINT
385   I=1
390   DISP "Press CONT to begin data aquisition"
400   PAUSE
410   OUTPUT 9;"U1G"!Start the clock
420   DISP "PRESS K7 TO TERMINATE DATA GATHERING"
430   CARD ENABLE 7!Allow DVM interupts to take place.
440   IF I<1000 THEN GOTO 440
450   DISABLE
```

```
460   PRINTER IS 16
470   PRINT "ALLOCATED CORE STORAGE IS FULL"
480   PRINTER IS 0
490   GOSUB End
500 Exit:   OUTPUT 701;"*"
505   STOP
510 Read:     ! INPUT DATA FROM DSC
520   ENTER 701;Y(I)
525   Y(I)=Y(I)*1000+20 !Convert millivolts to a 0 to 10 scale.
530   OUTPUT 9;"U1V"
540   ENTER 9;Time
550   Temp(I)=Time*Rate/1000+Tinit
560   PRINT USING 570;Temp(I),Y(I),I
570   IMAGE DDDDXXXXXXXXXXXXXXX,MDD.DDXXXXXXXX,DDDD
590   I=I+1
650   OUTPUT 701;"@"
660   CARD ENABLE 7
670   RETURN
680 End:  !  Process Data
685  Y(1)=Y(2)  !Bad data point eliminator
690   Temp(1)=Tinit !Make sure first point is correct
700   Npts=I-2  !Eliminate extraneous data points
710   REDIM Y(Npts),Temp(Npts)  !Condense the arrays.
720   Minimum=FNMin(Y(*),Npts)  !Calculate lowest voltage output from DSC.
730   MAT Y=Y-(Minimum) !Set zero point as lowest output voltage
770   CALL Graph(A$,B$,Temp(*),Y(*),Npts)
780   LINPUT "DO YOU WANT THE DATA STORED?",C$
790   IF C$[1,1]="Y" THEN CALL Store(A$,B$,Temp(*),Y(*),Npts,Tinit,Rate,Samplema
ss,Sensitivity)
800   LINPUT "DO YOU WANT TO EXPAND THE PLOT",D$
810   IF D$[1,1]="Y" THEN CALL Expand(A$,B$,Temp(*),Y(*))
820   LINPUT "DO YOU WANT TO MAKE A LINEAR BASELINE CORRECTION?",E$
830   IF E$[1,1]="Y" THEN CALL Transform(A$,B$,Temp(*),Y(*),Npts)
835   PRINTER IS 16
836   PRINT PAGE
837   PRINT "Peak integrator using an arbitrary baseline correction"
838   PRINT
839   PRINT "Data point numbers correspond to origional data list"
840   PRINT LIN(2)
841   PRINT "The baseline is calculated using a staight line from the first to
the last data point"
842   PRINT LIN(3)
843   PRINT "Press STOP if you wish to terminate the program.  Press CONT if
you    wish to continue."
844   PAUSE
845   PRINT PAGE
848   INPUT "ENTER BEGINNING AND ENDING POINTS FOR NUMERICAL INTEGRATION",Begin,
End
850    Qpts=End-Begin+1
852    PRINT USING 854;Qpts
854    IMAGE "ENTER 1 AND ",DDD," FOR INTEGRATION LIMITS"
856    REDIM X3(Qpts),Y3(Qpts)
858    FOR L=1 TO Qpts
860    Y3(L)=Y(L+Begin-1)
862    X3(L)=Temp(L+Begin-1)
864    NEXT L
866    Slope3=(Y3(Qpts)-Y3(1))/(X3(Qpts)-X3(1))
867    B=Y3(1)
868    FOR L=1 TO Qpts
870    Y3(L)=Y3(L)-Slope3*(X3(L)-X3(1))-B
872    NEXT L
874    C$=B$&":  Expanded plot peak integration"
876    CALL Graph2(A$,C$,X3(*),Y3(*),Qpts,Area)
878    LINPUT "DO YOU WANT TO CONTINUE WITH KINETICS?",Stop$
880   IF Stop$[1,1]<>"Y" THEN GOSUB Exit
881   CALL Kinetics(A$,C$,X3(*),Y3(*),Qpts,Area)
```

```
884   GOTO 300
885 Escape:  ! Correct any run errors.
890   PRINTER IS 16
900   PRINT ERRM$;" GENERATED.  EDIT PROGRAM AND PRESS CONT."
910   PAUSE
920   PRINTER IS 0
930   RETURN
1000  SUB Store(A$,B$,X(*),Y(*),N,T0,R,Sm,Sens)
1010  OPTION BASE 1  !Subroutine for storing data from X-Y plotter input.
1015  SHORT R(N),S(N)
1020  LINPUT "ENTER MASS STORAGE MEDIUM",F$
1030  LINPUT "ENTER 6 CHARACTER FILE NAME",G$
1040  G$=G$&":"&F$
1050  CREATE G$,N/9
1060  ASSIGN #2 TO G$
1070  PRINT #2;A$,B$,N,T0,R,Sm,Sens
1075  MAT R=X
1076  MAT S=Y
1080  MAT PRINT #2;R,S
1090  PRINT LIN(5)
1100  PRINT "DATA IS STORED IN FILE "&CHR$(34);G$;CHR$(34)
1110  ASSIGN #2 TO *
1120  SUBEXIT
1130  SUBEND
1200  SUB Graph(A$,B$,X(*),Y(*),N)
1201  OPTION BASE 1
1205  INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
1206  IF Code=2 THEN GOTO 1270
1210  PRINT PAGE     !Subroutine for plotting data from an X-Y plotter
1220  PRINT LIN(3)  !using the internal thermal printer.
1240  PRINT A$
1250  PRINT B$
1260  PRINT LIN(3)
1270  DIM C$[60],D$[60]
1275  LINPUT "ENTER X AXIS LABEL IF OTHER THAN TEMPERATURE (K)",C$
1276  IF C$="" THEN C$="TEMPERATURE (K)"
1277  LINPUT "ENTER Y AXIS LABEL IF DESIRED",D$
1278  IF D$="" THEN D$="Relative Millivolts"
1280  F=FNMax(Y(*),N)
1290  B=X(N)-X(1)
1300  A=F
1310  LINPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MAXIMUM",J$
1320  IF J$[1,1]="Y" THEN INPUT "ENTER Ymax",H
1330  IF J$[1,1]="Y" THEN A=H
1340  IF Code=2 THEN PLOTTER IS 7,5,"9872A"
1350  IF Code=1 THEN PLOTTER IS "GRAPHICS"
1360  GRAPHICS
1370  LOCATE 15,90,15,75
1380  SCALE X(1),X(N),0,A
1390  AXES B/4,A/10,X(1),0
1400  MOVE X(1),Y(1)
1410  FOR I=1 TO N
1420  DRAW X(I),Y(I)
1430  NEXT I
1440  PENUP
1480  LORG 6
1490  FOR I=X(1) TO X(N) STEP B/4
1500  MOVE I,-A/100
1510  LABEL USING 1530;I
1520  NEXT I
1530  IMAGE DDD
1540  LORG 8
1550  FOR I=A/10 TO A STEP A/10
1560  MOVE -B/100+X(1),I
1570  LABEL USING 1590;I
```

```
1580  NEXT I
1590  IMAGE DD.D
1600  LORG 6
1610  MOVE B/2+X(1),-A/15
1620  LABEL TRIM$(C$)
1630  LDIR PI/2
1640  LORG 4
1650  MOVE -B/10+X(1),A/2
1660  LABEL TRIM$(D$)
1670  PAUSE
1680  IF Code=1 THEN DUMP GRAPHICS
1690  EXIT GRAPHICS
1700  GCLEAR
1710  SUBEXIT
1720  SUBEND
1730  DEF FNMax(A(*),N)
1740  Max=A(1)
1750  FOR I=2 TO N
1760  IF A(I)>Max THEN Max=A(I)
1770  NEXT I
1780  RETURN Max
1790  FNEND
2000 SUB Expand(C$,D$,X(*),Y(*))
2010  OPTION BASE 1
2020  DIM Z(1000),T(1000),R(1000),W(1000)
2025  DIM I$[80],R$[80]
2030  INPUT "ENTER LOWEST AND HIGHEST DATA POINTS FOR PLOT EXPANSION (P1,P2)",P1
,P2
2040  N=ABS(P2-P1)+1
2050  REDIM Z(N),T(N)
2060  FOR I=1 TO N
2070  Z(I)=X(I+P1-1)
2080  T(I)=Y(I+P1-1)
2090  NEXT I
2100  I$=D$&"-EXPANDED PLOT"
2110  LINPUT "IS THIS A BASELINE CORRECTED PLOT?",M$
2120  IF M$[1,1]<>"Y" THEN GOTO 2175
2130  IF M$[1,1]="Y" THEN CALL Printz(C$,I$,Z(*),T(*),N)
2140  IF M$[1,1]="Y" THEN CALL Graph2(C$,I$,Z(*),T(*),N,Area)
2141  PRINTER IS 16
2143  PRINT "DO YOU WANT TO INTEGRATE THIS EXPANDED PLOT USING ANOTHER BASELINE
CORRECTION?"
2144  LINPUT N$
2145  PRINT PAGE
2146  IF N$[1,1]<>"Y" THEN GOTO 2170
2147  INPUT "ENTER THE DATA POINT NUMBERS (new list) FOR ORDINATE POINTS ",P3,P4
2148  Mx=P4-P3+1
2149  REDIM R(Mx),W(Mx)
2150  PRINT USING 2152;Mx
2152  IMAGE "USE 1 AND ",DDD," FOR INTEGRATION LIMITS"
2153  FOR K=1 TO Mx
2154  R(K)=Z(K+P3-1)
2155  W(K)=T(K+P3-1)
2156  NEXT K
2157  R$="Expanded plot:  Arbitrary Baseline correction for curve integration."
2158  Slope2=(W(Mx)-W(1))/(R(Mx)-R(1))
2159  Bb=W(1)
2162  FOR K=1 TO Mx
2163  W(K)=W(K)-Slope2*(R(K)-R(1))-Bb
2164  NEXT K
2165  CALL Graph2(C$,R$,R(*),W(*),Mx,Area)
2170  IF M$[1,1]="Y" THEN SUBEXIT
2175  CALL Graph(C$,I$,Z(*),T(*),N)
2180  SUBEXIT
2185  SUBEND
2190  SUB Transform(F$,G$,X(*),Y(*),N)
```

```
2200  OPTION BASE 1  ! Linear baseline correction for 2 variable plots.
2210  DIM Ynew(N)
2212  INPUT "ENTER POINT NUMBER TO BEGIN BASELINE CORRECTION",Qpt
2215  DIM H$[80]
2220  S=(Y(Qpt)+Y(Qpt+1)+Y(Qpt+2))/3 ! Average three points
2230  V=(Y(N)+Y(N-1)+Y(N-2))/3  ! for slope calculation.
2240  Slope=(V-S)/(X(N)-X(1))
2250  FOR I=1 TO N
2260  Ynew(I)=Y(I)-Slope*(X(I)-X(1))-S
2270  NEXT I
2280  H$=G$&":Linear baseline correction"
2290  CALL Graph2(F$,H$,X(*),Ynew(*),N,Area)
2330  LINPUT "DO YOU WANT THE PLOT EXPANDED?",N$
2335  IF N$[1,1]="Y" THEN CALL Expand(F$,H$,X(*),Ynew(*))
2340  SUBEXIT
2350  SUBEND
2400 DEF FNMaxabs(A(*),N)
2410  Max=ABS(A(1))
2420  FOR I=2 TO N
2430  IF ABS(A(I))>Max THEN Max=ABS(A(I))
2440  NEXT I
2441  RETURN Max
2442  FNEND
2450 DEF FNMin(B(*),N)
2460  Min=B(1)
2470  FOR I=2 TO N
2480  IF B(I)<Min THEN Min=B(I)
2490  NEXT I
2500  RETURN Min
2510  FNEND
2600  SUB Graph2(A$,B$,X(*),Y(*),N,Integral)
2601  OPTION BASE 1
2605  PRINTER IS 0
2610  INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
2615  IF Code=2 THEN GOTO 2670
2620  PRINT PAGE      !Subroutine for plotting data from an X-Y plotter
2630  PRINT LIN(3)  !using the internal thermal printer.
2640  PRINT A$
2650  PRINT B$
2660  PRINT LIN(3)
2670  DIM C$[80],D$[80],Ux(1000),Vy(1000)
2671  REDIM Ux(N),Vy(N)
2675  LINPUT "ENTER X AXIS LABEL IF OTHER THAN TEMPERATURE (K)",C$
2676  IF C$="" THEN C$="TEMPERATURE (K)"
2677  LINPUT "ENTER Y AXIS LABEL IF DESIRED",D$
2678  IF D$="" THEN D$="Relative Millivolts"
2680  F=FNMaxabs(Y(*),N)
2690  B=X(N)-X(1)
2700  A=F
2710  LINPUT "DO YOU WANT A MAXIMUM Y USED FOR THE GRAPH INSTEAD OF THE CALCULAT
ED MAXIMUM",J$
2720  IF J$[1,1]="Y" THEN INPUT "ENTER Ymax",H
2740  IF J$[1,1]="Y" THEN A=H
2750  IF Code=1 THEN PLOTTER IS "GRAPHICS"
2755  IF Code=2 THEN PLOTTER IS 7,5,"9872A"
2760  GRAPHICS
2770  LOCATE 15,90,15,75
2780  SCALE X(1),X(N),-A,A
2790  AXES B/4,A/10,X(1),0
2800  MOVE X(1),Y(1)
2810  FOR I=1 TO N
2820  DRAW X(I),Y(I)
2830  NEXT I
2840  PENUP
2880  LORG 6
2890  FOR I=X(1) TO X(N) STEP B/4
```

```
2900  MOVE I,-A/100
2910  LABEL USING 2930;I
2920  NEXT I
2930  IMAGE DDD
2940  LORG 8
2950  FOR I=-A TO A STEP A/10
2960  MOVE -B/100+X(1),I
2970  LABEL USING 2990;I
2980  NEXT I
2990  IMAGE MDD.D
3000  LORG 6
3010  MOVE B/2+X(1),-A/15
3020  LABEL TRIM$(C$)
3030  LDIR PI/2
3040  LORG 4
3050  MOVE -B/10+X(1),A/2
3060  LABEL TRIM$(D$)
3062  LINPUT "DO YOU WANT TO INTEGRATE PART OF THE CURVE",O$
3065  IF O$[1,1]<>"Y" THEN GOTO 3085
3066  INPUT "ENTER BEGINNING AND ENDING DATA POINT NUMBERS(FROM NEW SET IF EXPAN
DED)",Start,Finish
3067  REDIM Ux(Finish-Start+1),Vy(Finish-Start+1)
3068  J=1
3069  FOR I=Start TO Finish
3070  Ux(J)=X(I)
3071  Vy(J)=Y(I)
3072  MOVE X(I),Y(I)
3073  DRAW X(I),0
3074  PENUP
3075  J=J+1
3076  NEXT I
3077  Epsilon=1E-6
3078  CALL Intun(J-1,Epsilon,Ux(*),Vy(*),Integral)
3079  PRINT USING 3080;Ux(1),Ux(J-1),Integral
3080  IMAGE "THE AREA REPRESENTED BY THE SHADED REGION BETWEEN DOMAIN VALUES  ",
DDDD.DD,"   AND ",DDDD.DD," IS  ",MD.DDDE
3081  PRINT LIN(2)
3085  LINPUT "DO YOU WANT GRAPHICS PRINTOUT VIA THE THERMAL PRINTER?",L$
3090  IF (L$[1,1]="Y") AND (Code=1) THEN DUMP GRAPHICS
3095  EXIT GRAPHICS
3100  GCLEAR
3110  SUBEXIT
3120  SUBEND
3130  SUB Printz(A$,B$,X(*),Y(*),N)
3140  OPTION BASE 1
3150  PRINT PAGE
3160  PRINT "DATA POINT RENUMBERING FOR BASELINE CORRECTED , EXPANDED PLOT"
3170  PRINT A$
3180  PRINT B$
3190  PRINT
3200  PRINT "DOMAIN VALUE      RANGE VALUE      NEW DATA POINT NUMBER"
3210  PRINT
3220  FOR I=1 TO N
3230  PRINT USING 3250;X(I),Y(I),I
3240  NEXT I
3250  IMAGE DDDD.DDXXXXXXXXXXX,DD.DDXXXXXXXXX,DDD
3260  PRINT LIN(6)
3270  SUBEXIT
3280  SUBEND
3400 SUB Intun(N,Eps,X(*),Y(*),Int) ! Cubic Spline Integrator
3480 Baddta=(N<=3) OR (X(1)>=X(N)) OR (Eps<=0)
3490 IF Baddta=0 THEN 3600
3520 PRINT LIN(2),"ERROR IN SUBPROGRAM Intun."
3530 PRINT USING 3540;N,Eps,X(1),X(N)
3540 IMAGE "N=",DDD,5X,"Eps=",MD.6DE, , "X(1)=",MD.6DE,5X,"X(N)=",MD.6DE,
3550 PAUSE
```

```
3500 GOTO 3480
3600 OPTION BASE 1
3610 DIM B(2:N-1),S(N),G(2:N-1)
3620 FOR I=2 TO N-1
3630    H=X(I+1)-X(I-1)
3640    X=X(I)-X(I-1)
3650    B(I)=.5*X/H
3660    T=((Y(I+1)-Y(I))/(X(I+1)-X(I))-(Y(I)-Y(I-1))/X)/H
3670    S(I)=2*T
3690    G(I)=3*T
3690 NEXT I
3700 S(1)=S(N)=0
3720 W=8-4*SQR(3)
3740 U=0
3760 FOR I=2 TO N-1
3770    T=W*(-S(I)-B(I)*S(I-1)-(.5-B(I))*S(I+1)+G(I))
3780    H=ABS(T)
3800    IF H>U THEN U=H
3820    S(I)=S(I)+T
3830 NEXT I
3850 IF U>=Eps THEN 3740
3860 Int=0
3920 FOR I=1 TO N-1
3930    H=X(I+1)-X(I)
3940    Int=Int+(.5*H*(Y(I)+Y(I+1))-1/24*H^3*(S(I)+S(I+1)))
3950 NEXT I
3960 SUBEND
4000  SUB Kinetics(A$,B$,X(*),Y(*),N,Area) !Nonisothermal DSC Kinetics
4010  OPTION BASE 1
4015  ON ERROR GOSUB Trap
4020  DIM Logd(N),Fract(4:N),Temp(N),A(4:N),D(N),Dfract(5:N),C(N)
4030  CALL Printz(A$,B$,X(*),Y(*),N)
4040  PRINT PAGE
4050  PRINT LIN(2)
4060  PRINT A$
4070  PRINT B$
4080  PRINT "Kinetics determination"
4090  PRINT
4100  PRINT "Temp(K)    1/T    Area Fract.    LN(ordinate)    Relative R
ate  Pr#"
4110  PRINT
4130  MAT Temp=(1)/X ! Calculate 1/T(K)
4132  FOR I=1 TO N    !INSURE NON NEGATIVE ARGUMENT
4134  IF Y(I)<=1 THEN GOTO 4140
4136  Logd(I)=LOG(Y(I))
4138  GOTO 4145
4140  Logd(I)=0
4145  NEXT I
4180  FOR I=1 TO 3  !SET UP ARRAYS
4190  C(I)=X(I)
4200  D(I)=Y(I)
4210  NEXT I
4220  Epsilon=1E-6
4230  FOR I=4 TO N !CALCULATE PARTIAL AREAS
4235  REDIM C(I),D(I)
4240  C(I)=X(I)
4250  D(I)=Y(I)
4270  CALL Intun(I,Epsilon,C(*),D(*),Partial_area)
4280  Fract(I)=Partial_area/Area
4285  DISP Partial_area,Fract(I),I
4290  NEXT I
4300  FOR I=5 TO N
4310  Dfract(I)=(Fract(I)-Fract(I-1))/(C(I)-C(I-1))
4320  NEXT I
4330 FOR I=5 TO N
4340  PRINT USING 4360;X(I),Temp(I),Fract(I),Logd(I),Dfract(I),I
```

```
4350  NEXT I
4355  PRINT
4360  IMAGE  DDDDXXXX,D.DDEXXX,Z.DDDXXXXXXXXXX,MD.DDDXXXXXXXXXXX,D.DDEXXXX,DDD
4370  ! PLOT Dfract vs Fract AND CHOOSE LINEAR SECTION FOR KINETICS
4380  PRINT PAGE
4390  PRINT LIN(3)
4400  PRINT "Kinetics plot of dx/dT vs x.  x = fraction decomposed"
4410  PRINT LIN(3)
4440  C=FNMaxy(Dfract(*),N)
4450  D=FNMinv(Dfract(*),N)
4460  E=.1
4470  F=(C-D)/10
4475  INPUT "ENTER PLOTTER CODE: 1=CRT; 2=9872A",Code
4480  IF Code=1 THEN PLOTTER IS "GRAPHICS"
4485  IF Code=2 THEN PLOTTER IS 7,5,"9872A"
4490  GRAPHICS
4500  LOCATE 15,90,15,75
4510  SCALE 0,1,D,C
4520  AXES .2,2*F,0,D
4530  FOR I=5 TO N
4540  MOVE Fract(I),Dfract(I)
4550  LABEL "+"
4560  NEXT I
4570  LORG 6
4580  FOR I=0 TO 1 STEP .2
4590  MOVE I,D-.1*F
4600  LABEL USING "Z.DDD";I
4610  NEXT I
4620  LORG 8
4630  FOR I=D+2*F TO C STEP 2*F
4640  MOVE -.01,I
4650  LABEL USING "D.DDE";I
4660  NEXT I
4670  LORG 6
4680  MOVE .5,D-.3*F
4690  LABEL "Fraction Decomposed"
4700  LDIR PI/2
4710  MOVE .025,D+5*F
4720  LABEL "Relative Rate"
4730  LDIR 0
4740  PAUSE
4750  IF Code=1 THEN DUMP GRAPHICS
4760  GCLEAR
4770  EXIT GRAPHICS
4780  PRINT PAGE
4790  PRINT LIN(2)
4800  PRINT "LINEAR REGRESSION ANALYSIS OF DATA"
4810  PRINT LIN(2)
4820  INPUT "ENTER BEGINNING AND ENDING POINTS FOR CALCULATION",Begin,End
4830  Pts=End-Begin+1
4840  REDIM T2(Pts),F2(Pts)
4850  IMAGE "Plot is between temperatures ",DDDD," and ",DDDD," Kelvin"
4860  FOR I=1 TO Pts
4861  T2(I)=Temp(Begin+I-1)
4862  F2(I)=Logd(Begin+I-1)
4965  NEXT I
4866  PRINT USING 4850;1/T2(1),1/T2(Pts)
4870  PRINT
4880  CALL Linear(T2(*),F2(*),Pts,A,B,C0,C1,C2,C3,C4,C5,C6,C7,C8,C9,V)
4890  PRINT USING 4900;-B*1.9872!Activation energy in cal./mole
4895  PRINT USING 4905;V
4900  IMAGE "Calculated activation energy (linear regression) is ",D.DDE," cal/m
ole"
4905  IMAGE "Mean slope variance is ",Z.DDDE," cal/mole"
4910  PRINT LIN(3)
4920  Xmax=FNMax2(T2(*),1,Pts)
```

```
4930  Xmin=FNMin2(T2(*),1,Pts)
4940  Ymax=FNMax2(F2(*),1,Pts)
4950  Ymin=FNMin2(F2(*),1,Pts)
4960  E=(Xmax-Xmin)/10
4970  F=(Ymax-Ymin)/10
4980  IF Code=1 THEN PLOTTER IS "GRAPHICS"
4985  IF Code=2 THEN PLOTTER IS 7,5,"9872A"
4990  GRAPHICS
5000  LOCATE 15,90,15,75
5010  SCALE Xmin,Xmax,Ymin,Ymax
5020  AXES 2*E,2*F,Xmin,Ymin
5030  FOR I=1 TO Pts
5040  MOVE T2(I),F2(I)
5050  LABEL "+"
5060  NEXT I
5070  FOR J=1 TO Pts
5080  F2(J)=B*T2(J)+A
5090  NEXT J
5095  MOVE T2(1),F2(1)
5100  FOR J=2 TO Pts
5110  DRAW T2(J),F2(J)
5120  NEXT J
5140  LORG 6
5150  FOR I=Xmin TO Xmax STEP 2*E
5160  MOVE I,Ymin-.1*F
5170  LABEL USING "D.DDD";I*1000
5180  NEXT I
5200  LORG 8
5210  FOR I=Ymin+2*F TO Ymax STEP 2*F
5220  MOVE Xmin-.04*E,I
5230  LABEL USING "MD.DDD";I
5240  NEXT I
5250  LORG 6
5260  MOVE Xmin+5*E,Ymin-F
5270  LABEL "1/T(K) x 1000"
5280  MOVE Xmin+.4*E,Ymin+5*F
5290  LDIR PI/2
5300  LABEL "ln (displacement)"
5310  PAUSE
5320  IF Code=1 THEN DUMP GRAPHICS
5330  GCLEAR
5340  EXIT GRAPHICS
5344  LINPUT "DO YOU WANT TO REPEAT THE CALCULATION?",Repeat$
5345  IF Repeat$[1,1]="Y" THEN GOTO 4780
5350  SUBEXIT
5351 Trap: DISP ERRM$
5352  PAUSE
5355  GOTO 4040
5360  DEF FNMaxy(X(*),N)
5370  Maxy=X(5)
5380  FOR I=5 TO N
5390  IF X(I)>Maxy THEN Maxy=X(I)
5400  NEXT I
5410  RETURN Maxy
5420  FNEND
5430  DEF FNMiny(X(*),N)
5440  Miny=X(5)
5450  FOR I=5 TO N
5460  IF X(I)<Miny THEN Miny=X(I)
5470  NEXT I
5480  RETURN Miny
5490  FNEND
5500  SUBEND
5700 SUB Linear(X(*),Y(*),N,A,B,Regss,Resss,Totalss,Regms,Resms,F,Dfreg,Dfres,Df
tot,Abort,Variance)
```

```
5710 ! *** MODEL: Y=A+B*X ***
5720 ON ERROR GOTO Bomb
5730 Abort=0
5740 Y1=X1=Z=X2=Y2=0
5750 FOR I=1 TO N
5760    X1=X1+X(I)              ! Sum of X's
5770    Y1=Y1+Y(I)              ! Sum of Y's
5780    X2=X2+X(I)*X(I)         ! Sum of X squares
5790    Y2=Y2+Y(I)*Y(I)         ! Sum of Y squares
5800    Z=Z+X(I)*Y(I)           ! Sum of XY's
5810 NEXT I
5820 X1=X1/N                    ! Mean X
5830 Y1=Y1/N                    ! Mean Y
5840 B=(Z-N*X1*Y1)/(X2-N*X1*X1)
5850 A=Y1-B*X1
5860 Totalss=Y2-N*Y1*Y1         ! Total Sum of Squares
5870 Regss=(Z-N*X1*Y1)^2/(X2-N*X1*X1)! Regression Sum of Squares
5880 Resss=Totalss-Regss        ! Residual Sum of Squares
5890 Regms=Regss                ! Regression Mean Squares
5900 Resms=Resss/(N-2)          ! Residual Mean Squares
5905 Variance=SQR(Resms/(X2-N*X1*X1))  ! Slope Variance
5910 OFF ERROR
5920 DEFAULT ON
5930 F=Regms/Resms              ! F Ratio
5940 DEFAULT OFF
5950 Dfreg=1                    ! Degrees of Freedom
5960 Dfres=N-2
5970 Dftot=Dfreg+Dfres
5980 SUBEXIT
5990 Bomb: Abort=1
6000 SUBEND
6010  DEF FNMax2(X(*),A,B)
6020  Max2=X(A)
6030  FOR I=A+1 TO B
6040  IF X(I)>Max2 THEN Max2=X(I)
6050  NEXT I
6060  RETURN Max2
6070  FNEND
6080  DEF FNMin2(X(*),A,B)
6090  Min2=X(A)
6100  FOR I=A+1 TO B
6110  IF X(I)<Min2 THEN Min2=X(I)
6120  NEXT I
6130  RETURN Min2
6140  FNEND
6200 SUB Polynomial(X(*),Y(*),N,Degree,Coeffs(*),Regss,Resss,Totalss,Regms,Resms
,F,Dfreg,Dfres,Dftot,Abort)
6210 ON ERROR GOTO Bomb
6220 Abort=0
6230 OPTION BASE 0
6240 DIM Matrix(Degree,Degree),Inv(Degree,Degree),B(Degree)
6250 REDIM Coeffs(Degree)
6260 IF Degree>N-2 THEN SUBEXIT  ! Check for higher degree than possible
6270 Dfreg=Degree
6280 Dfres=N-1-Degree
6290 Dftot=Dfreg+Dfres
6300 FOR K=0 TO Degree          !  Set up system of equations
6310    FOR J=K TO Degree
6320       Matrix(K,J)=0
6330       FOR I=1 TO N
6340          Matrix(K,J)=Matrix(K,J)+FNG(K)*FNG(J)
6350       NEXT I
6360    Matrix(J,K)=Matrix(K,J)
6370    NEXT J
6380    B(K)=0
6390    FOR I=1 TO N
```

```
6400        B(K)=B(K)+Y(I)*FNG(K)
6410     NEXT I
6420 NEXT K
6430 MAT Inv=INV(Matrix)          !  Solve the system of equations
6440 MAT Coeffs=Inv*B
6450 FOR I=1 TO N
6460  X1=X1+X(I)
6470  X2=X2+X(I)*X(I)
6480  Y1=Y1+Y(I)
6490  Y2=Y2+Y(I)*Y(I)
6500  Z=Z+X(I)*Y(I)
6510 NEXT I
6520 Y1=Y1/N
6530 X1=X1/N
6540 Totalss=Y2-N*Y1*Y1            ! Total Sum of Squares
6550 GOSUB Regss                   ! Regression Sum of Squares
6560 Resss=Totalss-Regss           ! Residual Sum of Squares
6570 Regms=Regss/Dfreg
6580 Resms=Resss/Dfres
6590 OFF ERROR
6600 DEFAULT ON
6610 F=Regms/Resms
6620 DEFAULT OFF
6630 SUBEXIT
6640 Regss: Regss=0
6650 FOR I=1 TO N
6660     J=0
6670     FOR L=0 TO Degree
6680        J=J+X(I)^L*Coeffs(L)
6690     NEXT L
6700     Regss=Regss+(J-Y1)^2
6710 NEXT I
6720 RETURN
6730 SUBEXIT
6740 DEF FNG(M)=X(I)^M
6750 Bomb: Abort=1
6760 SUBEND
6770  SUB Quad(X(*),Y(*),Z)
6780  PRINT LIN(2)
6785  OPTION BASE 1
6790  DIM A(3)
6800  CALL Polynomial(X(*),Y(*),Z,2,A(*),C0,C1,C2,C3,C4,C5,C6,C7,C8,C9)
6810  PRINT USING 6820;-A(2)*1.9872,A(1)*1.9872
6811  PRINT A(3)
6820  IMAGE "THE QUADRATIC COEFFICIENTS ARE ",MD.DDE," and ",MD.DDE
6830  PRINT
6840  SUBEXIT
6850  SUBEND
```

NOMENCLATURE

A	Total Area
a	Partial Area
$D(t)$	Ordinate Deflection
E^*	Activation Energy
$f(x)$	Algebraic Function of Fraction Reaction
G	Gibbs Free Energy
H	Enthalpy
$K(T)$	Equilibrium Constant
$k(T)$	Rate Constant
R	Universal Gas Constant
T	Temperature
T_m	Temperature of Maximum Exotherm
t	Time
X	Fraction Reacted
Z	Preexponential Factor in Arrhenius Equation
ϕ	Heating Rate

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